

PHOTOMETRIC TRACE ELEMENT ANALYSIS AND ITS APPLICATION TO THE INTERPRETATION OF NORWEGIAN GABBROID ROCKS

INAUGURAL DISSERTATION

zur

Erlangung des Doktorgrades
der Naturwissenschaftlichen Fakultät der
Johann Wolfgang Goethe Universität
zu Frankfurt am Main

vorgelegt von
Dettef Eugen Bodart
aus Konstanz

Frankfurt am Main

1970

Mit Genehmigung der Fakultät zum Druck
gekürzt. Ein Exemplar der ungekürzten
Arbeit liegt in der Senckenbergischen
Bibliothek der Universität vor.

PHOTOMETRIC TRACE ELEMENT ANALYSIS
AND ITS APPLICATION TO THE
INTERPRETATION OF NORWEGIAN GABBROID ROCKS

INAUGURAL DISSERTATION

zur

Erlangung des Doktorgrades
der Naturwissenschaftlichen Fakultät der
Johann Wolfgang Goethe Universität
zu Frankfurt am Main

vorgelegt von
Dettlef Eugen Bodart
aus Konstanz

Frankfurt am Main

1970

Mit Genehmigung der Fakultät zum Druck
gekürzt. Ein Exemplar der ungekürzten
Arbeit liegt in der Senckenbergischen
Bibliothek der Universität vor.

Gedruckt mit Genehmigung der Naturwissenschaftlichen
Fakultät der Universität Frankfurt am Main.



Dekan:-

Professor Dr.G. Schneider

Erster Berichterstatter:-

Professor Dr.K.v.Gehlen

Zweiter Berichterstatter:-

Professor Dr.K.R.Mehnert

Tag der mündlichen Prüfung:- 18.Juni 1970

DANKSAGUNG

Der Verfasser möchte sich für die ihm zugekommene Förderung in allen Bereichen, besonders für Ratschläge im Institut sowie im Gelände bei Herrn Professor Dr.K.v.Gehlen allerherzlichst bedanken.

Die grosszügige Bereitstellung von Mitteln zur Durchführung dieser Arbeit wurde unter der Verwendung von Sachbeihilfen der Deutschen Forschungsgemeinschaft an Herrn Professor v.Gehlen ermöglicht.

Der Verfasser möchte sich zusetzlich bei seinen Kollegen, Herrn M.Glaveris, R.Hindel und D.Taupitz für ausgezeichnete Zusammenarbeit, bei FrI.I.Pilger für ihre Hilfsbereitschaft, und bei Herrn G.Krause für Mitwirkung in der Herstellung mikroskopischer Präparate bedanken.



Digitized by the Internet Archive
in 2026

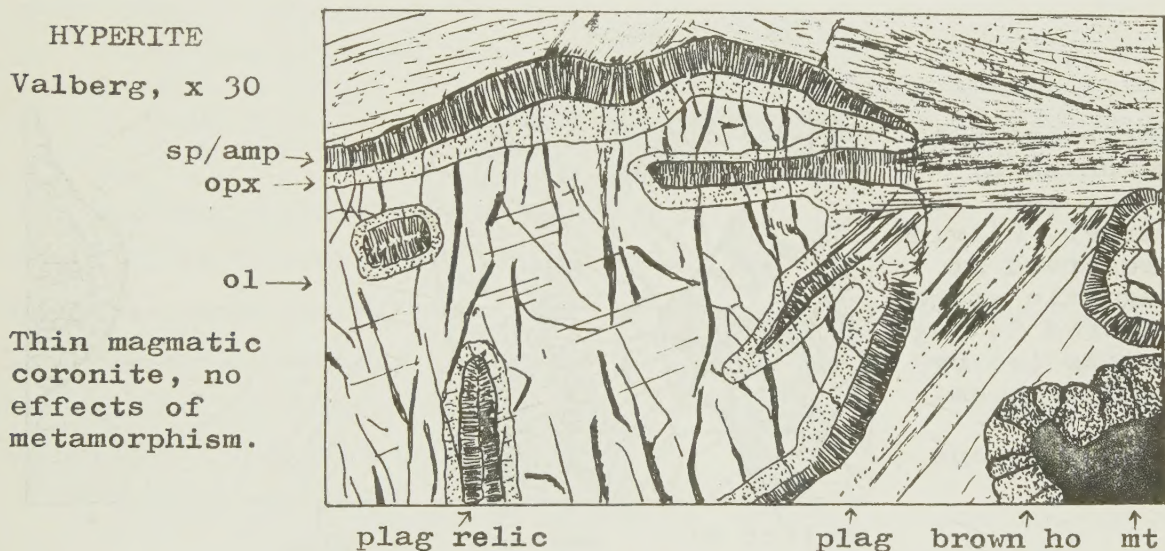
https://archive.org/details/IA41545305_0033

THE HYPERITE PROBLEM

The examination of silicate rocks by petrographic methods is often unreliable when the material in question is a product of multiple or re-crystallization sequences. This is due to the fact that such material can be expected as being the result of a long line of processes, the recognition and definition of which may in the absence of non-petrographic supplementary data be interpreted in a variety of ways.

A case in point is the genesis of HYPERITE. Mineralogically this rock contains a typically gabbroic mineral assemblage of olivine, pyroxene, hornblende, plagioclase and magnetite. REACTION ZONES enclosing olivine and magnetite however constitute a textural feature that sets this rock immediately aside from ordinary olivine-gabbros:-

HYPERITE
Valberg, x 30



The alteration of olivine and magnetite originates at crystal borders, and by progressing both out- and inwards from them leads to a multi- (olivine) or mono-zonal (magnetite) sheath described two-dimensionally as REACTION ZONE/RIM, KELYPHITIC RIM, or CORONITE. The mineral assemblages within these coronites, normally composed of pyroxenes, spinels and amphiboles in the case of olivine, and brown hornblende in the case of magnetite, follow definitive patterns, and may be developed to an extent so as to replace the original mineral completely:-

OLIVINE RELICS

x 30

opx →

sp →

amp →

Advanced mag-
matic stage.
Relic = coro-
nite.



↑
plag

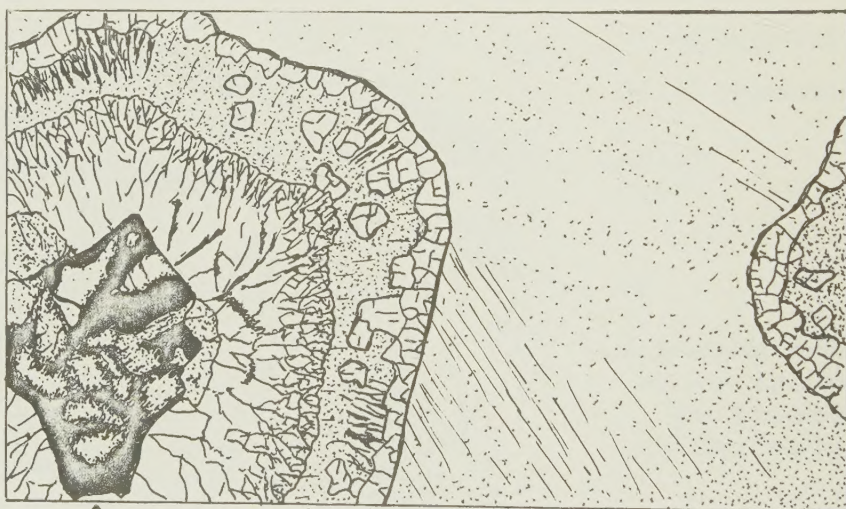
An apparent complicating factor has long been the inclusion of typically metamorphic minerals such as garnet, common hornblende and secondary magnetite within, and usually within definitive zones of these coronites:-

HYPERITE

Hönstjern, x 30

Incipient meta-
morphism of
outer zone to
garnet. Olivine
preserved at
magmatic stage,
altered to mag-
netite (+) by
metamorphism.

opx →



↑
relict ol

↑
amp

↑
gt

↑
plag

Coronar Gabbros (Hyperites) are of restricted, though world-wide distribution, and constitute in spite of extensive if regionally restricted petrographic study, a controversial phenomenon that has so far remained unexplainable by basic, accepted mechanisms of rock formation. Sederholm (1916) considered coronites a product of metamorphic alteration, as all occurrences recognized as hyperites were restricted to Pre-Cambrian metamorphic terranes. The theory of such an origin was, especially as coronites appeared to be characterized by metamorphic minerals such as garnet, not seriously contested in the subsequent work of Brögger (1934), Shand (1945), Ellis (1946), Gjelsvik (1952), Huang and Merritt (1954), Friedmann (1955), Murthy (1958),

Starmer (1969) and Glaveris (1970).

Murthy (1958), although recognizing the necessity of OH-groups ("intergranular film of water") for the formation of the outer amphibole/spinel zone, considered coronite formation a result of:-

"Regional metamorphism at comparatively high temperatures under water deficient conditions, with little shearing stress".

Reynolds and Fredrickson (1962) reversed this order of importance in their description of the Valberg Hyperite in attributing water to have:-

"Played an extremely important role in the metamorphism of hyperites",

by acting as a carrier of ions as well as a catalyst for mineral transformations. The effects of metamorphism are on the other hand no longer considered all-important:-

"The temperature and pressure factors must have been favourable, but without the addition of water none of the reactions involving a hydroxyl phase would have been possible these conclusions are in agreement with the experimental findings of Yoder (1952, 1955)".

Frodesen (1969) in his examination of the Hiåsen Hyperite about 20 km southwest of Valberg, differentiated between the two zones by considering the inner orthopyroxene one a result of late magmatic residua activated by immediately subsequent metamorphism, while ascribing a purely metamorphic origin to the outer one of amphibole and spinel.

A metamorphic origin of a regular mineral assemblage as intricate as coronites would however seem contrary to established theory. Metamorphic alteration of olivine and magnetite is not only known to proceed along completely different lines, but would be expected to reduce, rather than increase the number of mineral phases. These doubts have been consolidated in the following geochemical study of hyperites and associated basic rocks from the Bamble Region in South Norway, where coronite formation has been studied previously in greater detail than elsewhere. This investigation brought to light geochemical anomalies in hyperites that explain the origin of coronites as a result of special conditions during magmatic evolution and intrusion.

METHODS OF ANALYSIS

A lack of speed, accuracy or simplicity of current analytical techniques has frequently resulted in restrictions of large-scale geochemical investigations to one element. The present system of RAPID PHOTOMETRIC TRACE ANALYSIS represents an attempt at reaching a compromise between these factors. Existing colorimetric methods were either adapted directly (Fe, Ti, P, Mn), modified (V, Cr, Cu), improved (Co), or newly developed (Ni). (Mg, Zn) and (Na, K, Ca) were determined by atomic absorption and flame emission methods respectively. 168 rock samples were analysed fully for all but the last three, and 84 mineral samples partly for the above components. This work, including the development of the analytical system (Bodart 1969, 1970) involved around 2600 solvent extractions and 1400 determinations in aqueous medium. Dissolution with acid was carried out on around 750, with alkali on around 200 samples. 230 thin sections were prepared for microscopic examination. A complete account is given in the original dissertation.

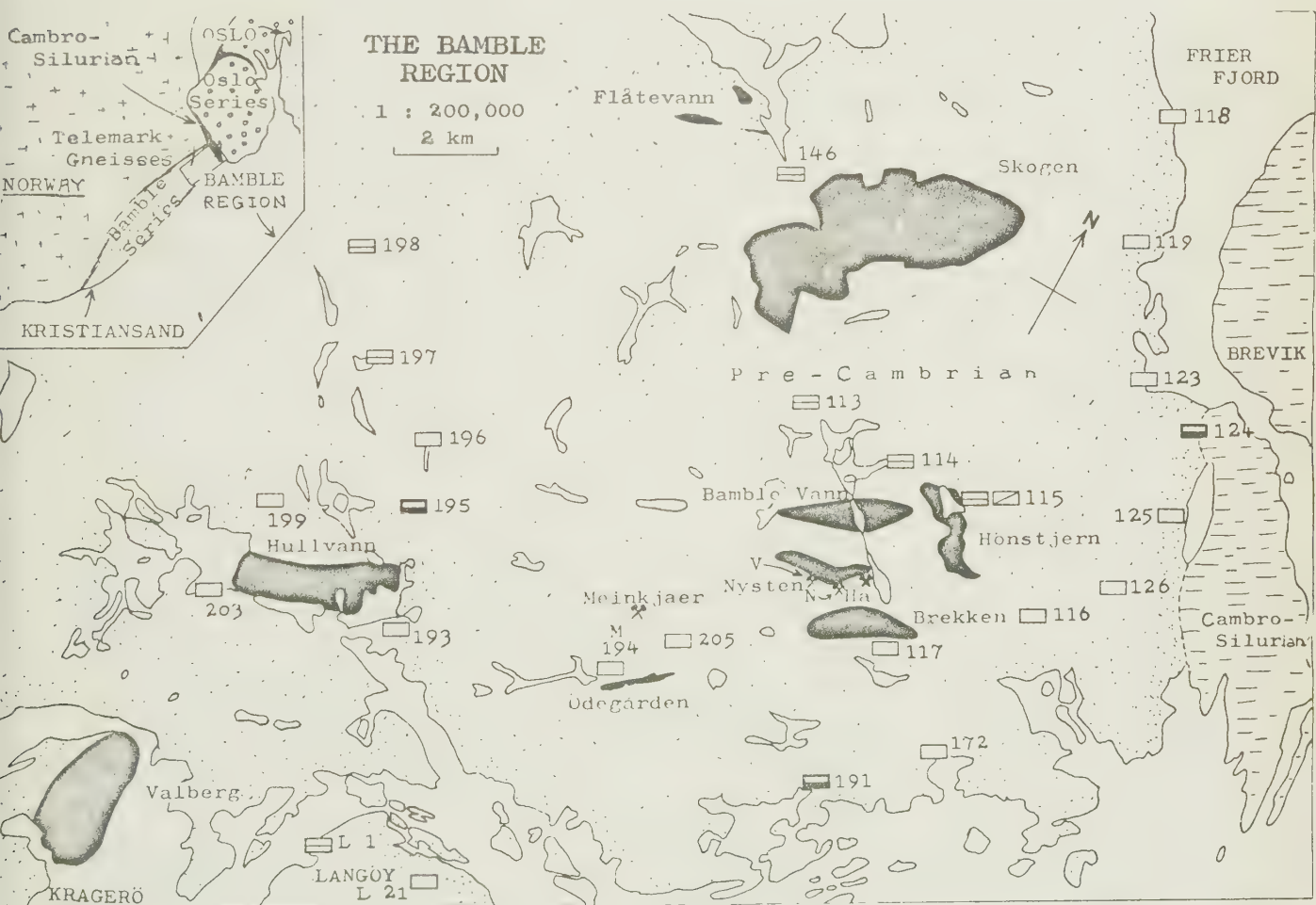
DISSOLUTION: 1 % rock solutions, suitable for most determinations, but diluted if necessary were prepared using $\text{H}_2\text{F}_2/\text{HClO}_4$ (for Mg, Fe, Mn, Ti, V, P); $\text{H}_2\text{F}_2/\text{HNO}_3$ (for Ni, Co, Cu, Zn) in PTFE dishes and $\text{Na}_2\text{CO}_3/\text{MgO}$ (for Cr) in Pt-crucibles. Sulphide and oxide ores were brought into solution by $\text{HCl}/\text{HNO}_3/\text{Br}$ in glass or $\text{K}_2\text{S}_2\text{O}_7$ in Pt-ware respectively.

COLORIMETRY:	<u>Chromophore</u>	<u>Medium</u>
Fe	1,10-phenanthroline	Aqueous
Ti	Titanyl sulphate	Aqueous
P	Phosphorvanadomolybdate	Aqueous
V	N-benzoyl-o-tolyl hydroxylamine	Carbon tetrachloride
Co	2-nitroso-1-naphthol	Iso-amyl acetate
Ni	Furildioxime	Chloroform
Cu	Neocuproine	Chloroform
Cr	Diphenylcarbazide	Aqueous

FLAME SPECTROMETRY: Mg and Zn were determined by Atomic Absorption Spectrophotometry at 202.6 and 213.9 nm using SrCl_2 and synthetic silicate rock buffers respectively. Na, K and Ca were determined in feldspars by Flame Photometry after the removal of R_2O_3 by precipitation from dilute $\text{H}_2\text{F}_2/\text{HClO}_4$ solutions.

THE BAMBLE REGION, SOUTH NORWAY.

The region covers only the northeastern part of the BAMBLE SERIES, a rock group forming the 140 x 20-30 km coastal strip between the rural community of Bamble in the north, and the town of Kristiansand in the south. This group is separated by the KRISTIANSAND-PORSGRUNN FAULT from the TELEMARK GNEISSES to the north, and ascribed to the Sveco-Norwegian Zone of the Baltic Shield with an age of 1200 - 900 m.y. It was formerly considered to represent a southern extension of the Kongsberg Series, 60 km to the north.



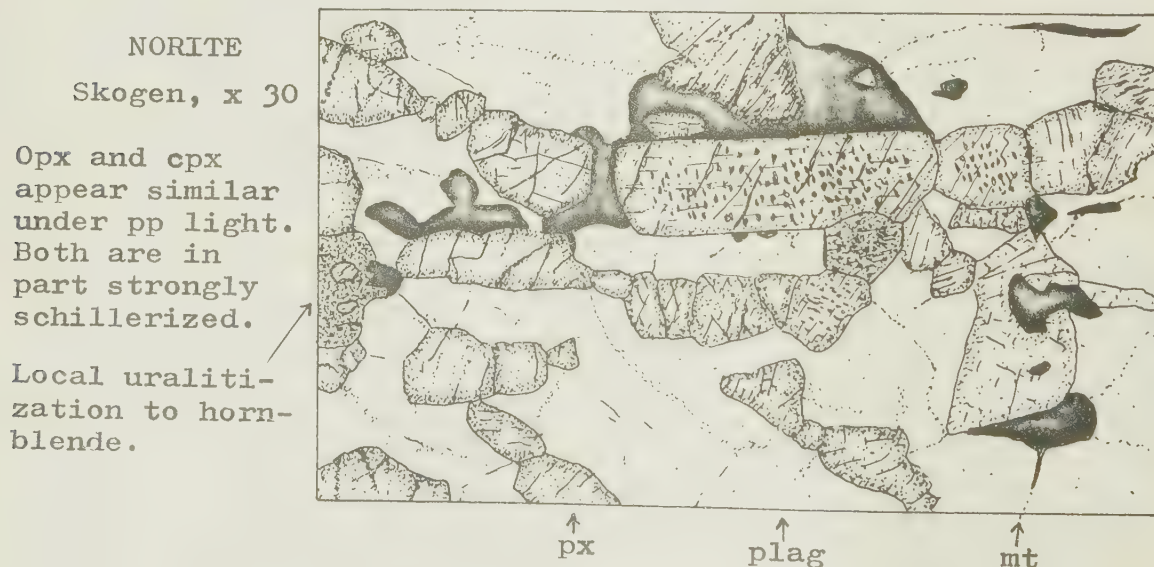
The BASIC ROCKS of the region and their quantitatively most important minerals are:-

GABBRO	HYPERITE	olivine/clinopyroxene/plagioclase
	NORITE	orthopyroxene/clinopyroxene/plagioclase
DOLERITE		pyroxene/plagioclase/magnetite
AMPHIBOLITE		hornblende/plagioclase

THE GABBROS: HYPERITE and NORITE

Both types of gabbro were intruded into the country rocks (amphibolite, granite gneiss, biotite schist, quartzite) from a generally accepted subjacent basalt magma reservoir between two metamorphic periods in the time interval 1200 - 900 m.y. They were already investigated in the middle of the last century by Forbes (Valberg Hyperite). Subsequent investigations within the Bamble Region and adjoining areas were carried out by Vogt (1893), Brögger (1934), A.Bugge (1936, 1965), J.Bugge (1943), Reynolds and Fredrickson (1962), Frodesen (1968), Starmer (1969) and Glaveris (1970). The area has been mapped on a scale of 1 : 15,000 by Batey (1965) and Ryan (1966).

Microscopic investigation of section material verified the results of previous workers. In the field HYPERITE (coarse-grained, melanocratic, feldspar lath-like and superficially purple-brown) is easily distinguished from NORITE (medium to coarse-grained, mesocratic, feldspar granular and superficially gray). This latter rock-type constitutes the bodies of Skogen, where it may be relatively unaltered and uniform over a wide area, and Nysten where it is extensively uralitized. Essential minerals are plagioclase, strongly schillerized ortho- and clinopyroxene (hypersthene, diallage) and magnetite.



The uralitized varieties at the Nysten Mass are directly (Mine Localities Nysten, Vissestad, Hansås) or probably indirectly (Mine Locality Meinkjaer) associated with NICKELIFEROUS SULPHIDE ORE deposits. Within these, two mineral associations, one BASIC containing hornblende and biotite with SULPHIDES

(pyrite, pyrrhotine-pentlandite, chalcopyrite) and one ACID with quartz, feldspar and biotite with OXIDE (magnetite) and SULPHIDES (pyrite, chalcopyrite) could be distinguished.

Analysis of pyrite (8 samples), pyrrhotine-pentlandite (16) and chalcopyrite (5) showed that the distribution of COBALT within these phases: py(2.55):po(0.094):cp(0.029) % are in accordance with the findings of Rost (1939) and Hegemann (1943). The comparatively large variation of cobalt in pyrite (0.15 - 5.21%) could not be correlated with the acid/basic mineral association: this might possibly have been expected from the proposed dependence of this value on the formation temperature (Björlykke and Jarp 1950). The NICKEL content of the pyrrhotine-pentlandite ore was, as is commonly the case, relatively constant, with an average of 4.4%. The gangue minerals gave on average: Magnetite (10 samples) Ti 1.67%, V 0.15%, Mn 0.19%: Biotite (9) Mg 4.23%, Fe 18.6%, Ti 2.12%, Mn 0.26%: Feldspar (15) AB/AN/OR = 71/24/5, Fe 0.65%. These values would indicate (magnetite Ti-poor, biotite Fe-rich, feldspar mostly oligoclase) a relatively low temperature of formation for the ACID quartzo-feldspathic association.

The mineral assemblages found in association with HYPERITES are characterized by their abundance of PHOSPHOROUS and locally TITANIUM. A small occurrence of ilmenite (8 samples) Ti 27.7% V 0.27% and Mn 0.32% was associated with feldspar (7) of AB/AN/OR = 82/16/2, Fe 0.76%, and pyrite (5) Co 0.35%, was found at the Road Metal Quarry within the Apatite Mines at Ödegården.

NON-GABBROIC BASIC ROCKS: AMPHIBOLITE and DOLERITE

The AMPHIBOLITES may be of ortho- or paragenic origin, and constitute together with granite-gneiss and subordinate biotite-schist and quartzite the basement rock. All gabbro masses have been altered locally, and especially in their marginal regions to a variety of amphibolite that is distinguishable from that of the basement only by way of its gabbroic geochemistry.

DOLERITES cross-cut older rocks, and are probably the youngest ones of the region. They were sampled only at one locality (124).

GEOCHEMICAL CRITERIA INVESTIGATED

Material was collected to cover three fundamental variables:-

DIFFERENCES IN GEOCHEMISTRY BETWEEN HYPERITE AND NORITE

The bodies of Hönstjern (18 samples), Bamble Vann (6) and Valberg (8) were composed essentially, those of Ödegården (6) Flåte vann (6) and Brekken (2) partly of hyperite. The bodies of Skogen (30) and Nysten (5) were essentially norite, although grading locally into a special type of hyperite.

GEOCHEMICAL VARIATION WITHIN A HYPERITE MASS

The high degree of differentiation possible is effectively shown by the medium-sized (2.7 x 0.8 km) mass at Hullvann (59 samples). This mass was further characterized by a special highly fractionated basic facies not examined elsewhere.

GEOCHEMISTRY OF COUNTRY ROCKS

The geochemistries of hyperite and norite were considered against a background of regional amphibolites (27 samples) and dolerite (1 sample).

QUANTITATIVE MEASURE FOR THE BASIC CHARACTER OF A GABBROIC ROCK

The problem of finding a suitable geochemical parameter for this entity is, especially in the case of basic rocks much simpler than in petrography. A commonly used, though without reference to Al_2O_3 and Mg:Fe ratio very subjective value is that of SiO_2 . More reliable are those of Mg and Ni. In the Bamble Region Mg is locally enriched near hyperites as cordierite-anthophyllite assemblages and Mg-amphiboles (Bodart 1966, 1968), while a small though insignificant amount of Ni can be present in all rocks as sulphide. The parameter finally chosen as an INDICATOR OF BASIC CHARACTER was the LOGARITHMIC VALUE OF NICKEL which, while easily determinable by a new method developed during the course of this investigation (Bodart 1969), not only exhibited a considerable range, but could also, as the element is readily accommodated in all mafic minerals, be considered independent of mineral constitution.

FRACTIONATION TRENDS OF HYPERITE AND NORITE

Considerable chemical variations exist within individual gabbro bodies; these follow accepted fractionation trends. Similar, albeit smaller variations exist between the averages of individual hyperite bodies. The elements examined were classified as follows:-

EARLY MAGMATIC	Ni, Mg, Co. Quantitative increase with basic character.
LATE MAGMATIC	Cu, Ti, V, P. Quantitative increase in later differentiates.
NON-DIFFERENTIATED	Fe, Mn, Zn. Pronounced fractionation not discernable. Approximately equal distribution.
IRREGULAR	Cr. Distribution irregular.

RELATIONSHIP OF PETROGRAPHY TO GEOCHEMISTRY

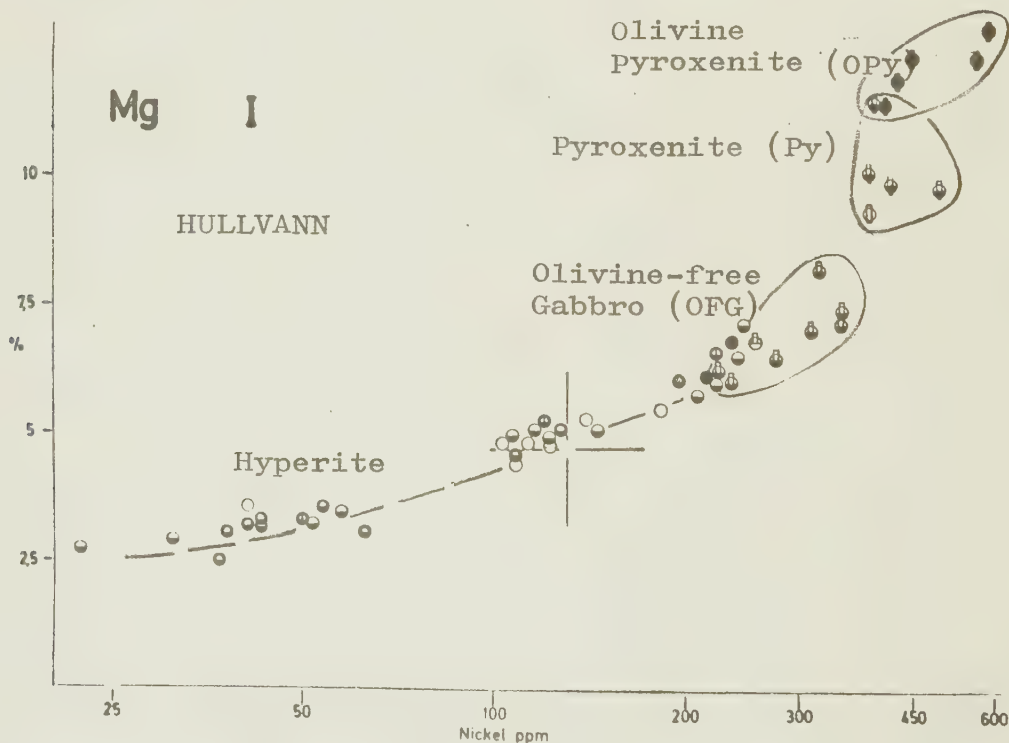
All material analysed was examined microscopically. The particular sign allocated to a sample represented a synthesis of locality (outer shape of sign) and mineral constitution (inner modification):-

LOCALITY		ROCK TYPE	
I. Hullvann	○	Hyperite	○
II. Skogen	□	Olivine-free Gabbro	○
Nysten	◇	Pyroxenite	○
Hönstjern	△	Special Rock	○
Bamble Vann	▽		
		MINERAL ASSEMBLAGE	
III. Valberg	⤿	Olivine	●
Flåtevann	▮	Orthopyroxene (primary)	◐
Ödegården	▮	Orthopyroxene (secondary)	◑
Brekken	▮	Clinopyroxene (primary)	◒
Regional Amphibolites and Dolerite	▮	Clinopyroxene (secondary)	◓
		Amphibole	○

Primary orthopyroxene includes clinopyroxene (= Norite); Olivine includes all other minerals.

EARLY MAGMATIC ELEMENTS

One of the most strongly fractionated of all elements is NICKEL. Its early removal from the magma of basic rocks is considered primarily due to the strong stabilization it can impart to the structure of early, forsteritic olivine (Edelshtein 1960) formed at high temperature (Häkli and Wright 1967). As crystallization proceeds, the amounts up to 2000 ppm present in such olivine will be reduced rapidly to below 100 ppm in the more fayalitic varieties, with the result that the less noted tenors - hornblende, orthopyroxene and augite respectively - will, albeit at a much reduced overall amount, incorporate a greater portion of the element. The validity of these criteria becomes evident when considering the Mg:logNi relationship of the differentiated hyperite at Hullvann:-



The most basic rocks at Hullvann are a product of GRAVITATIONAL

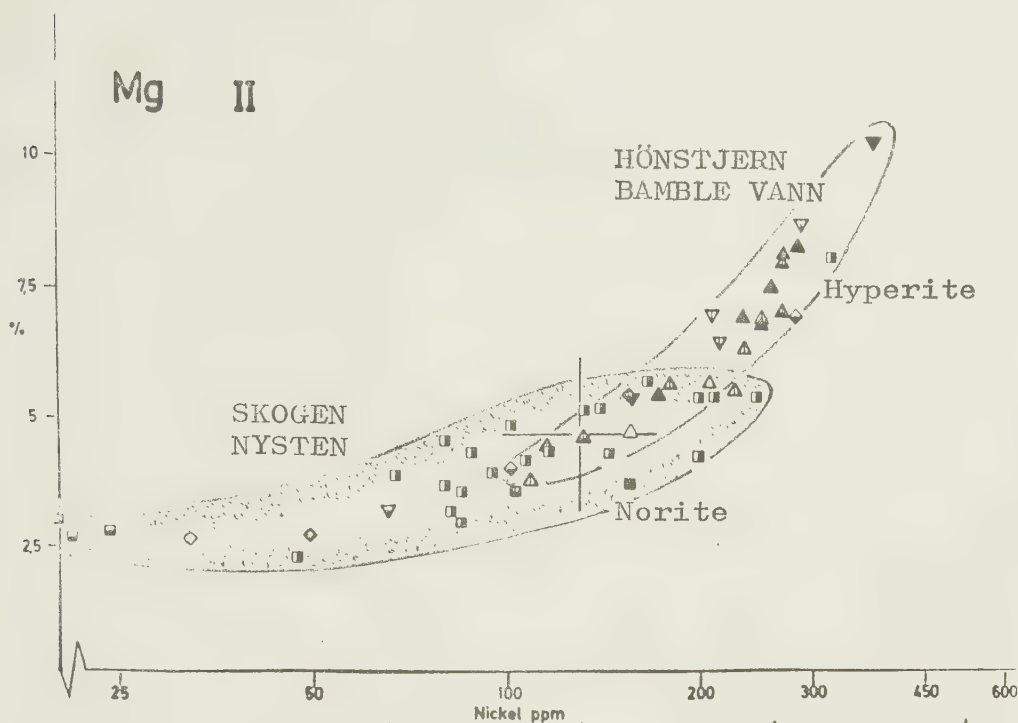
FRACTIONATION:- Olivine-free gabbro = pyroxene + feldspar

Pyroxenite = pyroxene

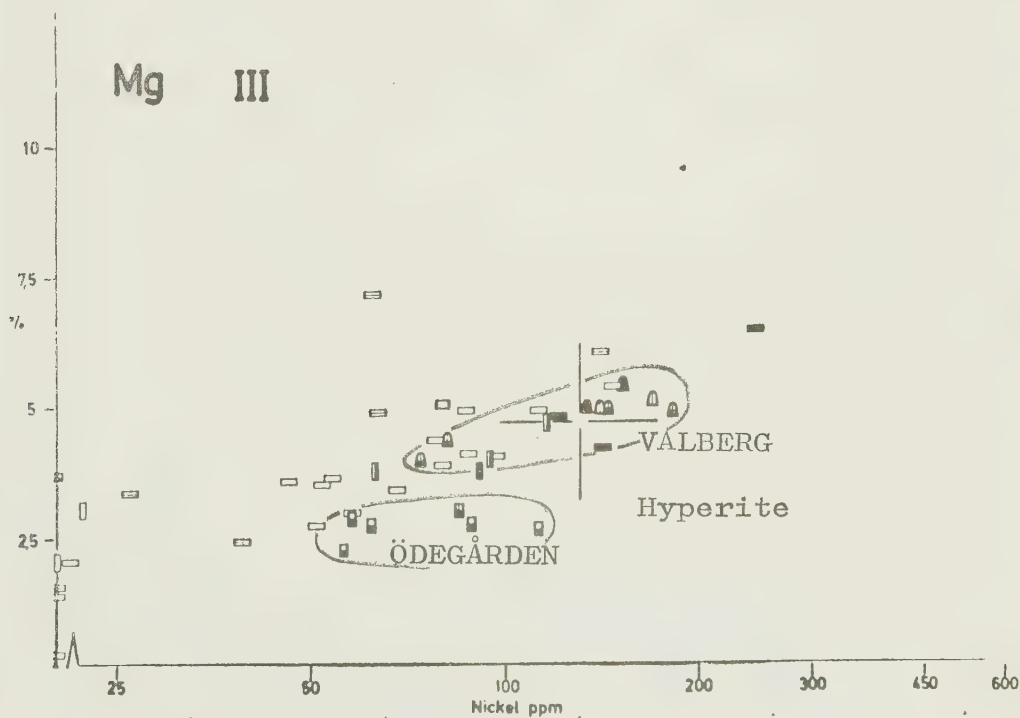
Olivine pyroxenite = pyroxene + olivine

Strongly uralitized ortho- and clinopyroxenes were common to all three rock types, while olivine and feldspar seemed mutually exclusive. All samples below 200 ppm Ni are hyperites. The regular trend exhibited by this material at all stages of alteration from pure hyperite to pure amphibolite demonstrates the stability of chemical- against the instability of mineral composition.

The norites at Eastern Bamble (Skogen/Nysten) appear less basic than the regionally associated hyperites:-



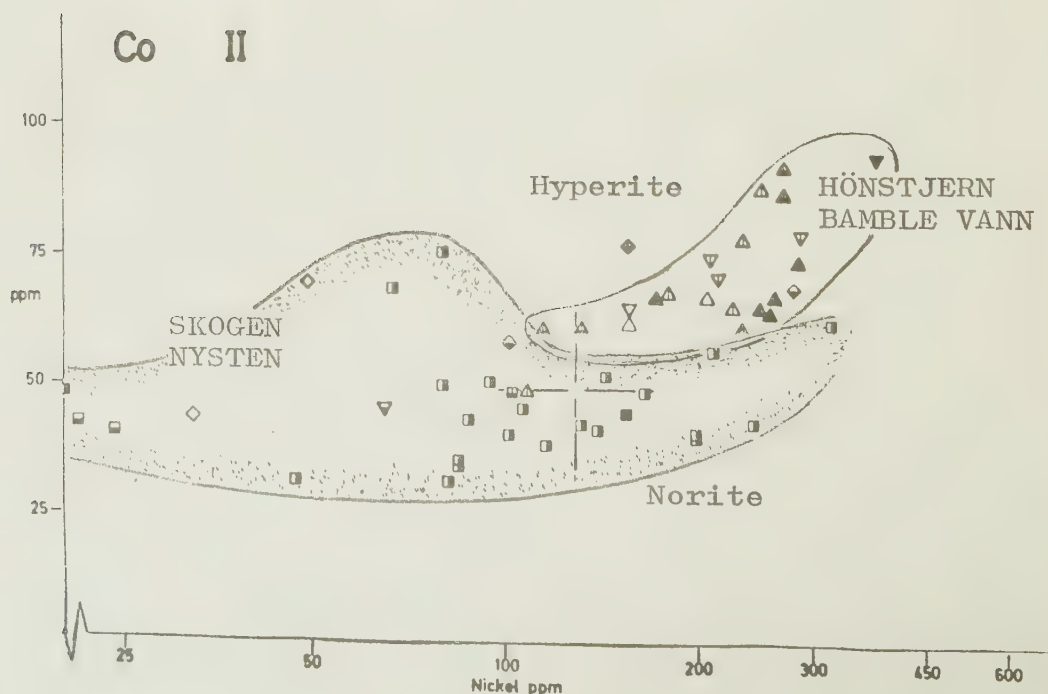
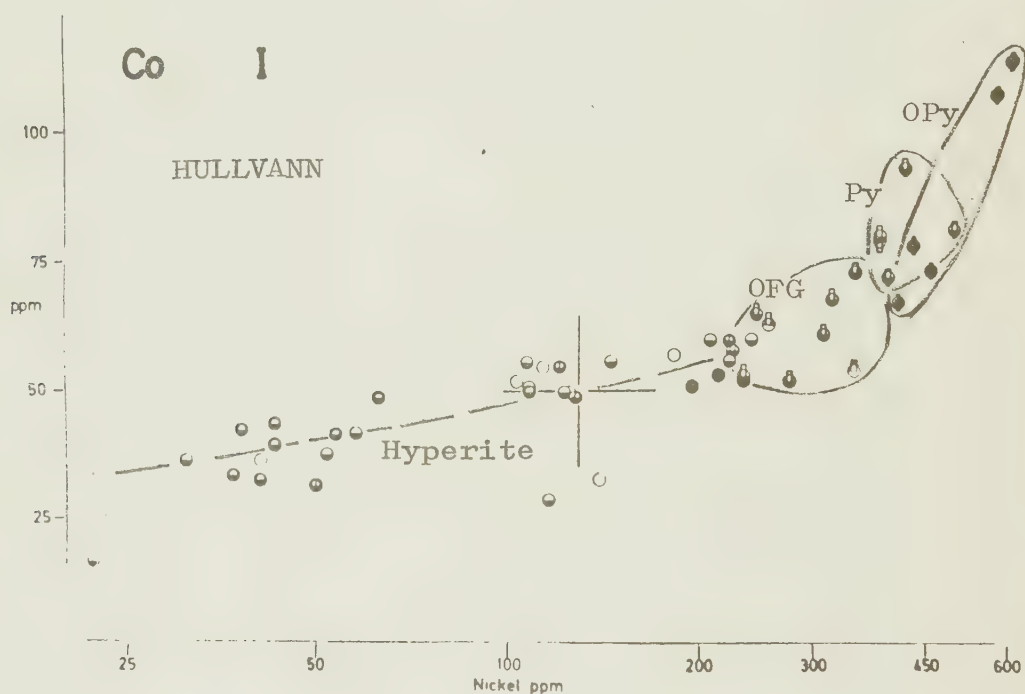
Both rock-types do however, as does the hyperite of Valberg follow the differentiation trend evident at Hullvann:-

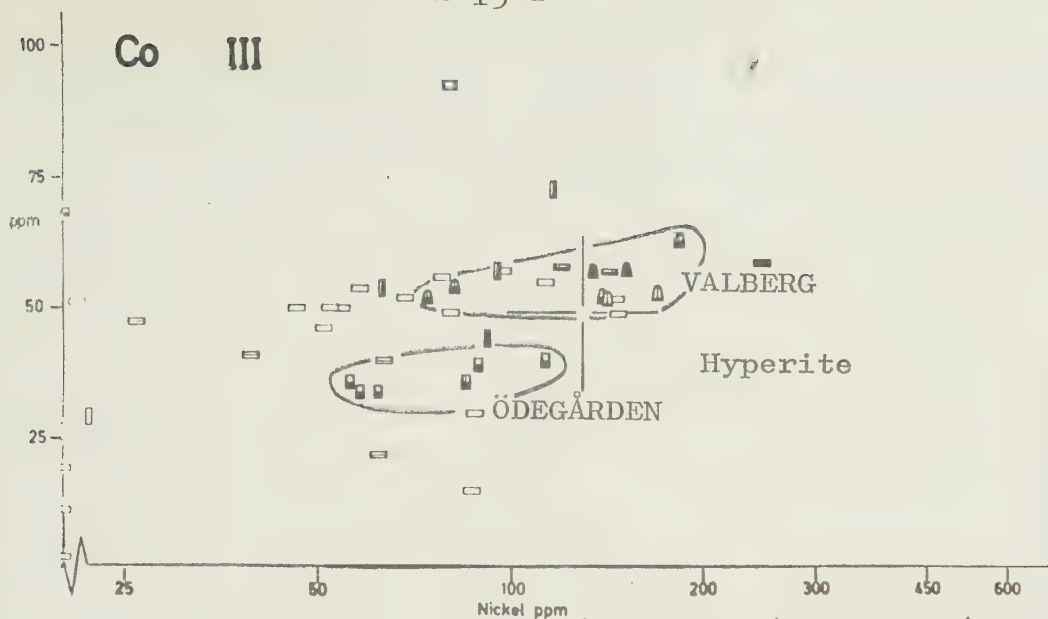


The samples from Ödegården are, with respect to their low Mg-content relatively enriched in Ni, a fact that could be attributed to their content of pyrrhotite-pentlandite. The otherwise very closely maintained Ni:Mg relationship does however prove that the amount of Ni bound to S in the gabbro itself can only be very small. This becomes evident from a consideration of the average 4.4% Ni of 16 pyrrhotite-pentlandite samples from

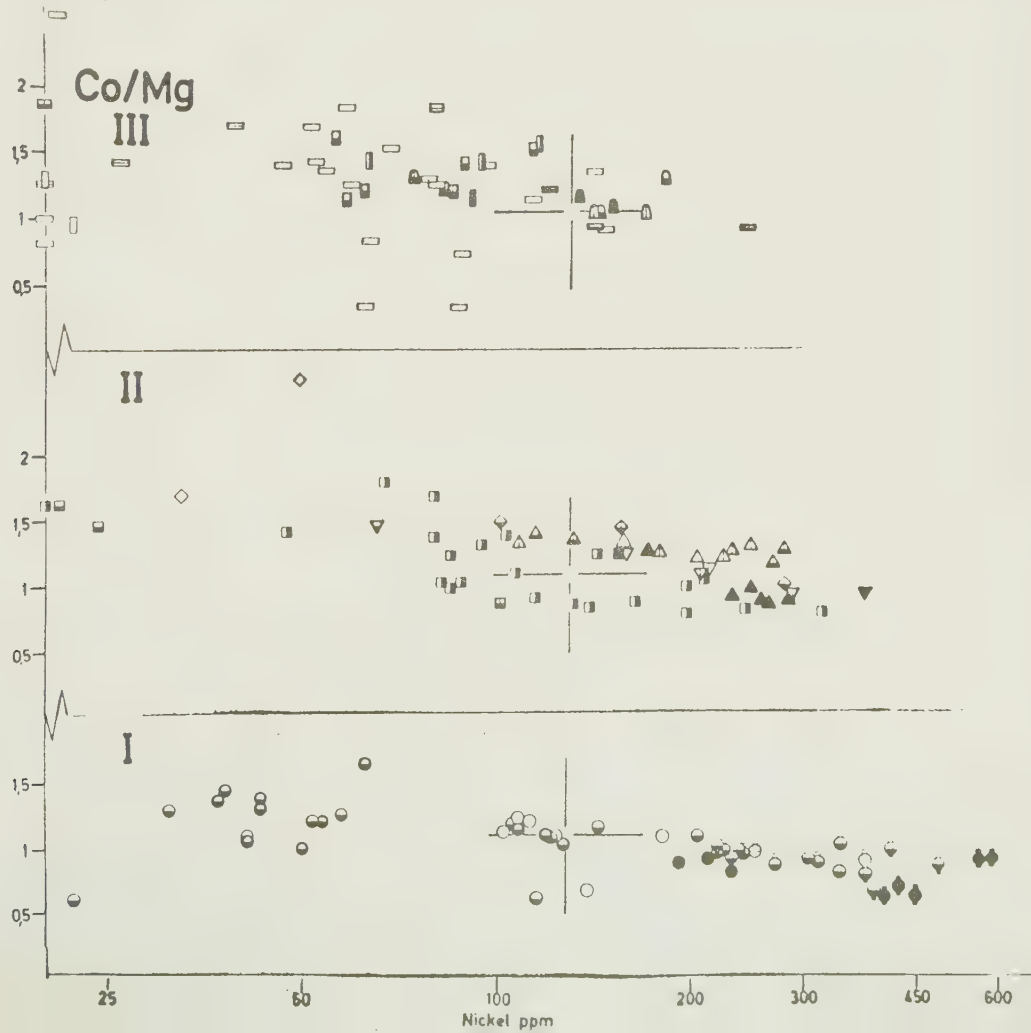
the Bamble localities with the overall low S-content of gabbros generally (< 500 ppm, of which >90% occurs as sulphide: Ricke 1960), as well as the only trace amounts of sulphide recognizable in petrographic study. The fact that the pyrrhotite-pentlandite ore bodies are here as on a world-wide basis either closely associated with (Nysten), or universally considered derived from (Skogen) norite, suggests that a certain amount of nickel must have been removed at some stage before consolidation of the rock.

The geochemical behaviour of COBALT bears a strong resemblance to that of magnesium:-





This may be primarily attributed to the similar FIELD FUNCTION of Ahrens (1964) (Ionization Potential/Ionic Radius = 23.1 for Mg^{2+} and 23.7 for Co^{2+}), a measure of the attractive strength of an ion on the lattice site of a growing crystal. The slightly higher field-function of Co should be weighed against the greater covalency in the bond with oxygen. It would be necessary to invoke this latter effect in any attempt made at explaining the regular impoverishment of Co respective to Mg with increasingly basic character:-

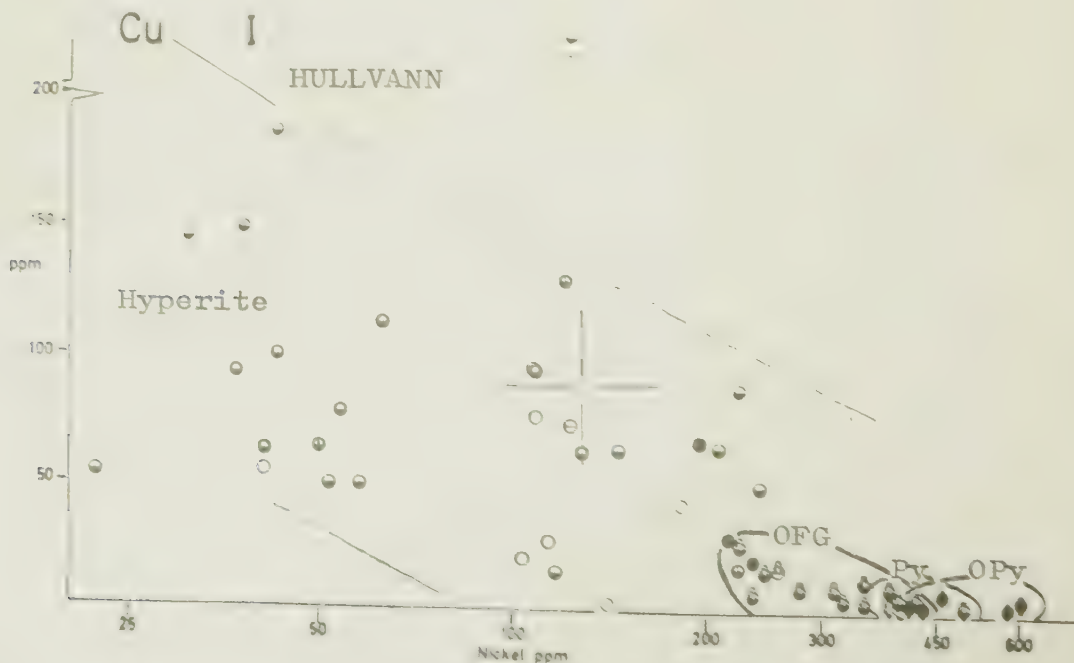


Of special interest are certain samples of amphibolite which, by falling outside this latter trend, might be of non-basaltic origin. The differences to Ni^{2+} (field function 26.3) are manifested by the very much smaller concentration range of the less highly fractionated, more lithophile Co. It thus follows that when both elements do increase in a linear fashion, factors other than chemical differentiation are responsible. Such is the case for the three closely associated rock types OLIVINE-FREE GABBRO, PYROXENITE and OLIVINE PYROXENITE from Hullvann: here an increase of 300 to 600 ppm Ni is met by an equivalent one of 55 to 110 ppm Co. This would indicate that these rocks represent stages of a gravitationally fractionated series, in which the minerals had crystallized before fractionation.

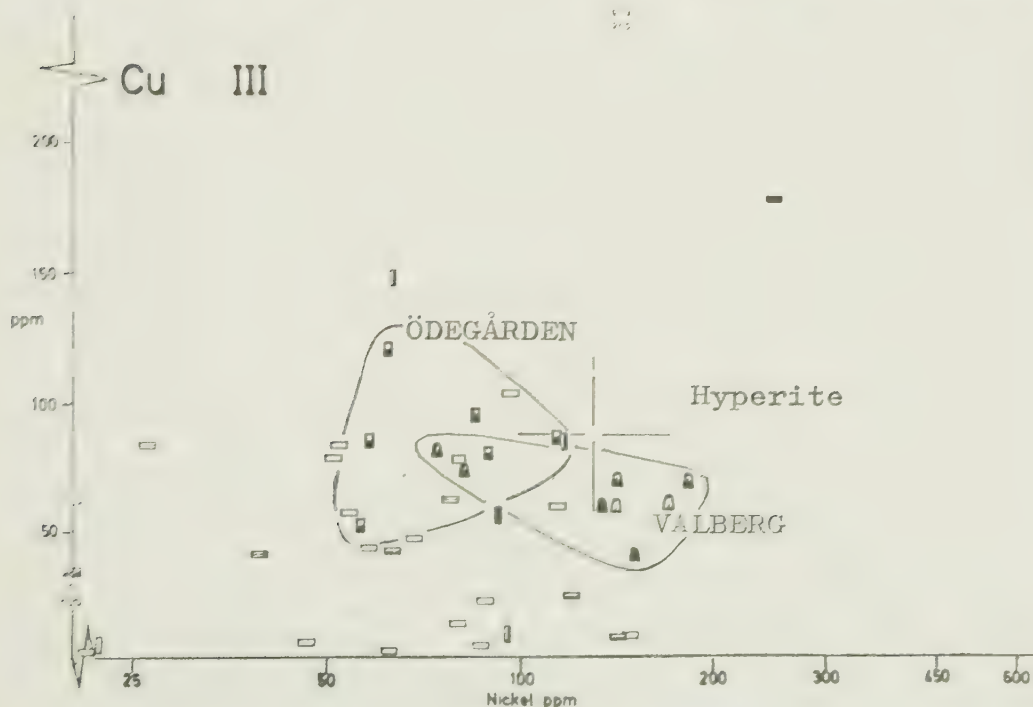
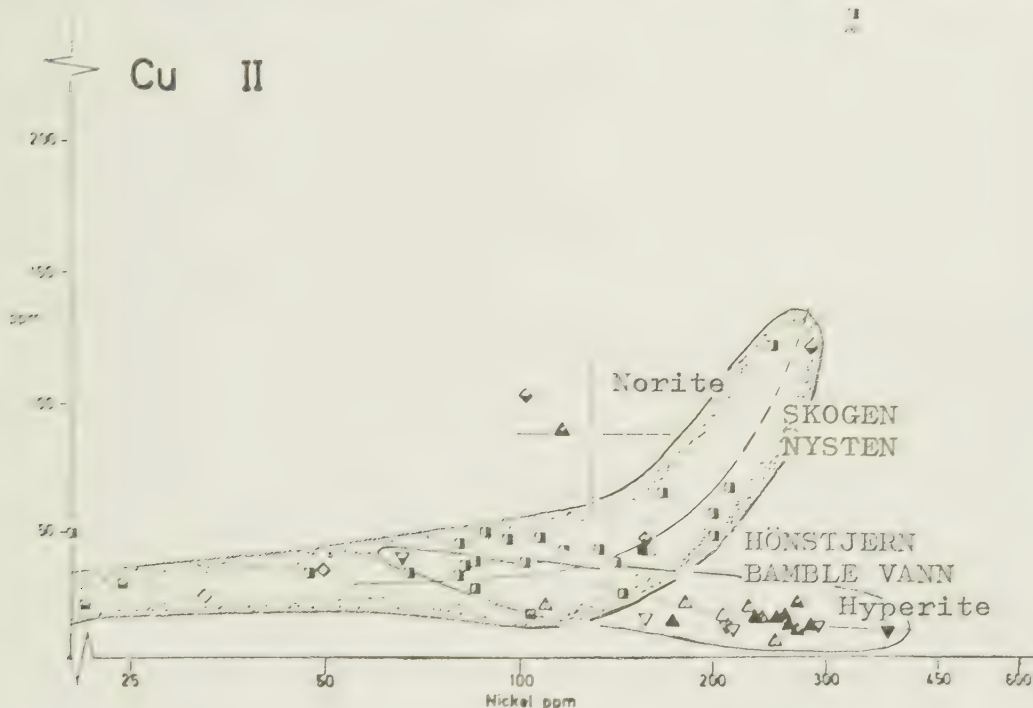
LATE MAGMATIC ELEMENTS

The elements Cu, Ti, V, and P are in spite of very different crystal chemistries, enriched in the less basic differentiates. This apparent similarity must be, Ti and V excepted, considered as coincidental, and due to a variety of unrelated factors.

The geochemistry of COPPER is governed by a strong affinity for S, coupled with reduced incorporation into common silicates. The latter fact, which has been ascribed both to a distorted structure and a weak Cu - O bond, is as expected most significant in the early silicates of hyperites, where the competition for lattice positions is highest:-



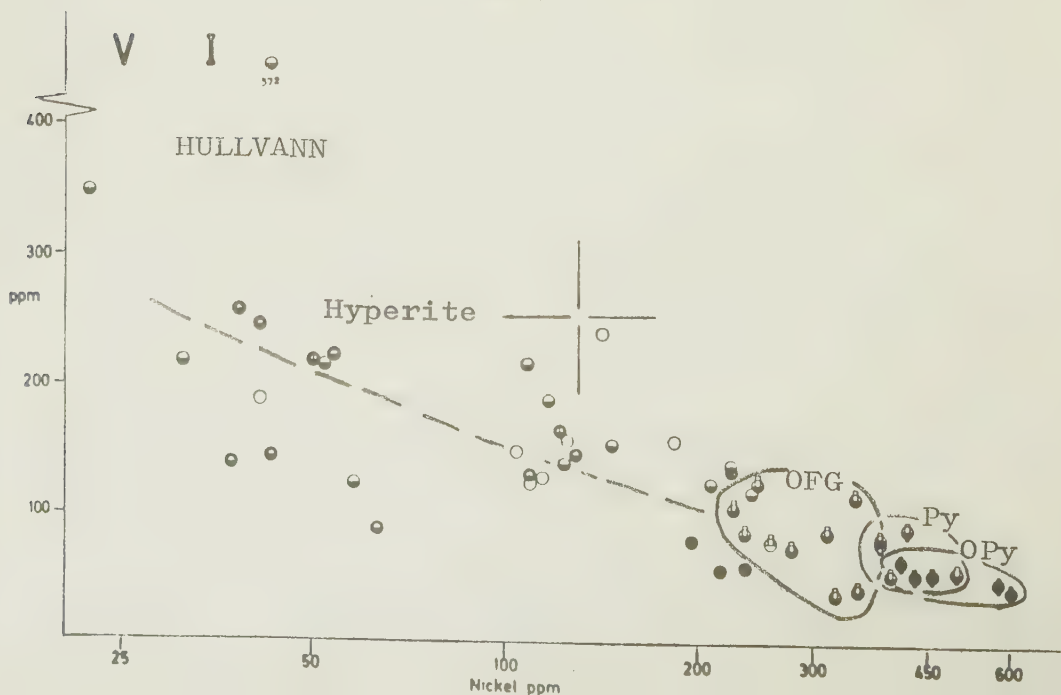
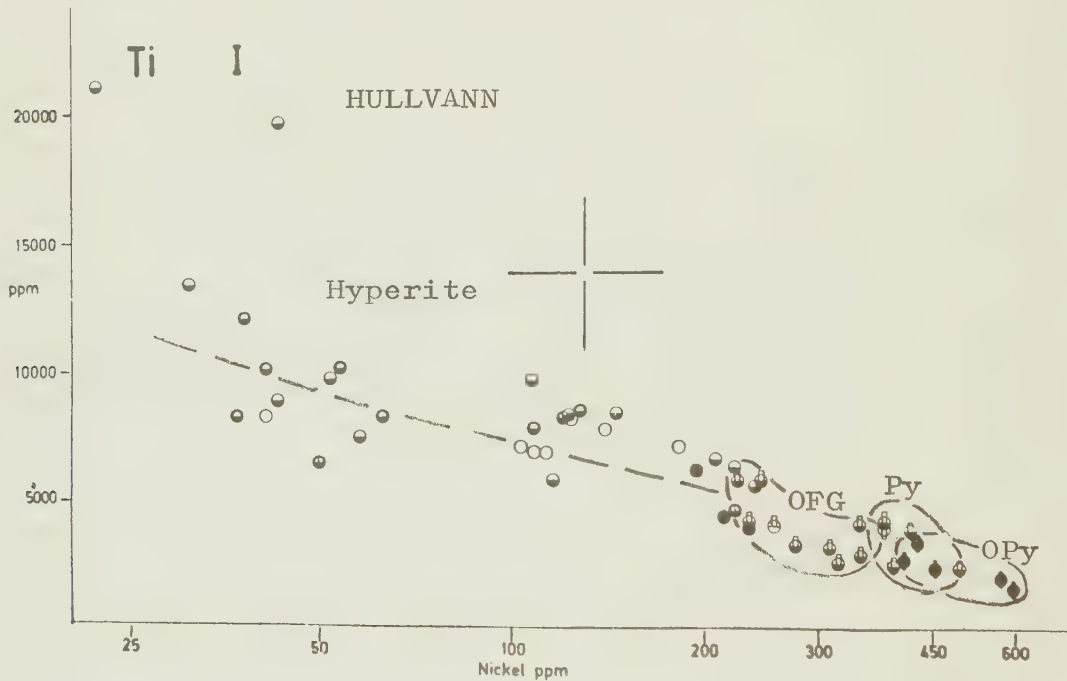
This is in full accordance with the low content of Cu in ultramafic rocks generally (10 ppm, Turekian and Wedepohl 1961). The indifference to silicate structures coupled with affinity for S might be taken to explain the sporadic distribution at higher values (Hullvann). As however a certain if limited amount is always incorporated into silicates, a more regular distribution would be expected when this is small (Hönstjern, Bamble Vann):-



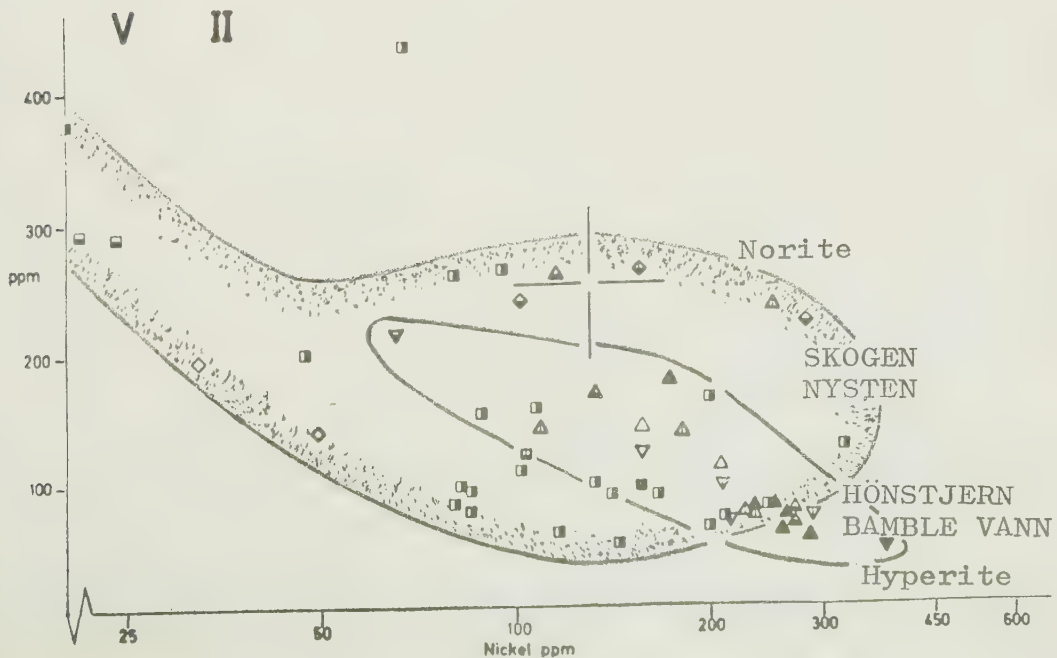
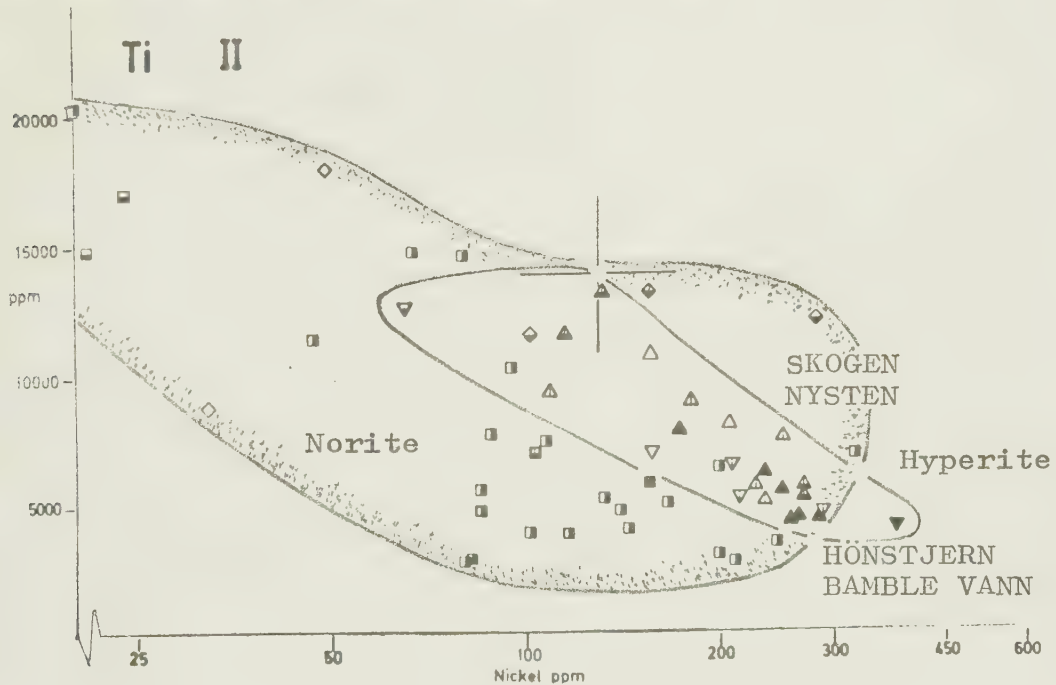
The increase of Cu with basic character in norites stands in strong contrast to the decrease in hyperites, being evidently governed by different geochemical principles. Here Cu follows

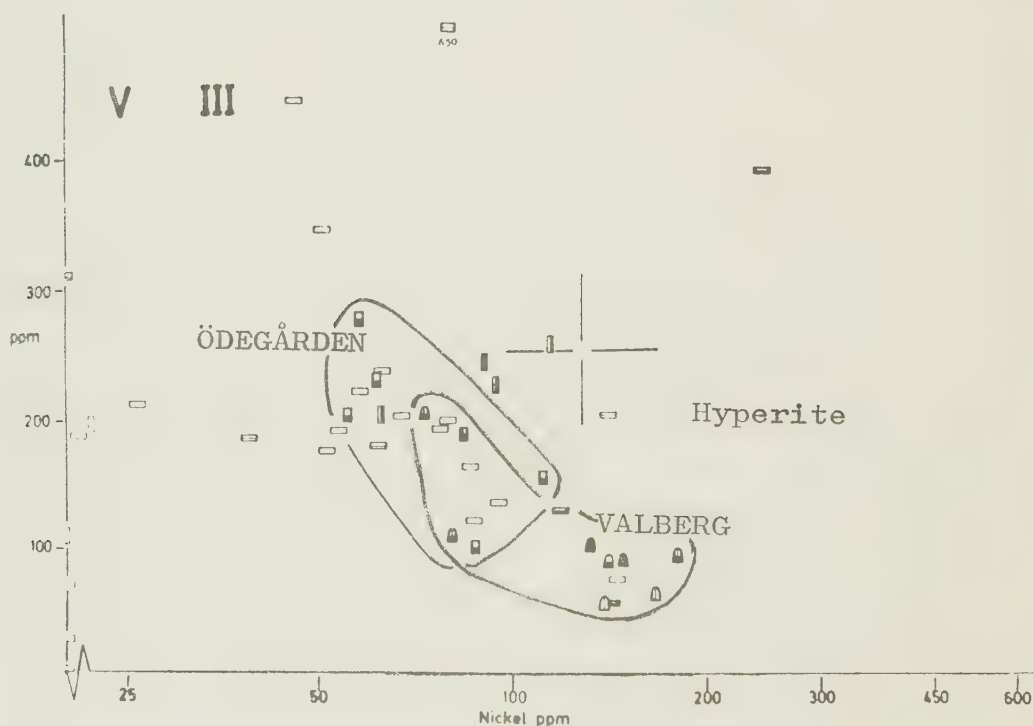
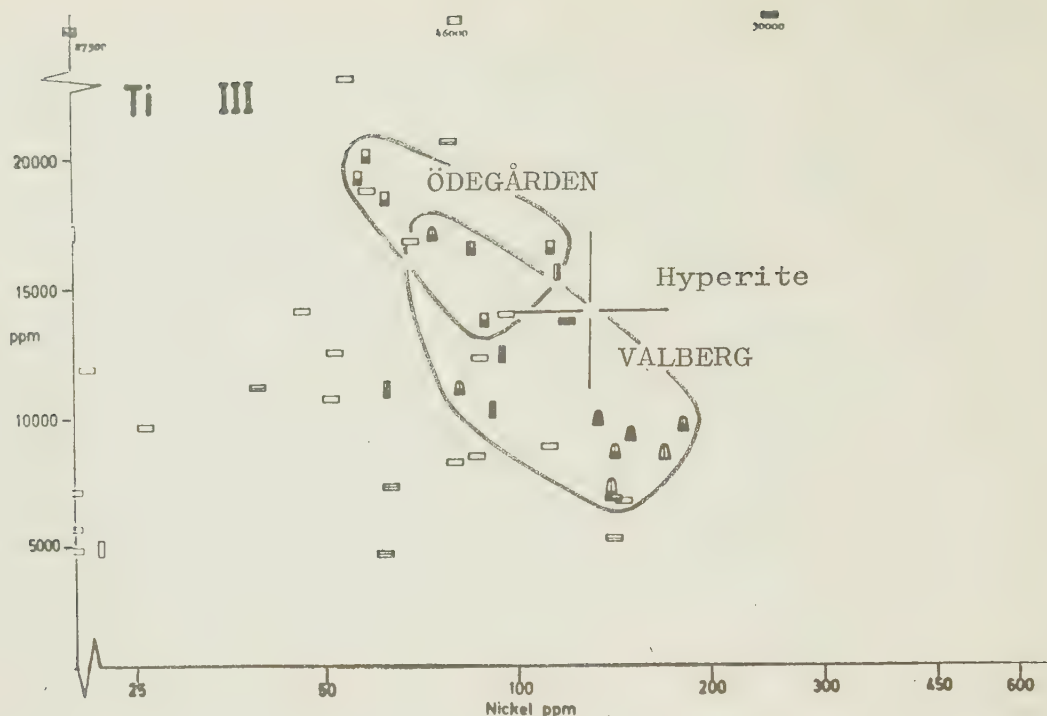
to some extent the path of Cr (p.26), leading to Cr:Ni:Cu relationships such as are possible in Hawaii Basalts (Wager and Mitchell 1953).

The geochemical analogy of TITANIUM and VANADIUM is primarily dependent on the type of rock in question. Ti, while incorporated into the mafic minerals of basic rocks, forms separate ones in acid magmas. V, bearing a greater geochemical resemblance to Fe, is at a much reduced overall amount (Ti:V ~ 50:1 in basaltic rocks), always incorporated into minerals of Fe and Ti. There are nevertheless certain restrictions based primarily on ionic charge that prevent the unrestricted substitution of Ti and V into ferromagnesian silicates. This leads to a similar impoverishment with basic character as found in Cu:-



The potential accomodation of Ti and V has been described as greatest in hornblende, and progressively less in co-existing clinopyroxene, orthopyroxene, and lastly olivine (Borisenko 1967, Mercy and O'Hara 1967). The role of these two elements in ferromagnesian silicates would appear to depend on lattice positions available to the trivalent ions Ti^{3+} and V^{3+} . Thus Taylor (1965) considers the substitution of V^{3+} for Fe^{2+} extremely limited in olivine, although high values of Ti are occasionally reported for this mineral (Tilley 1952, Muir 1954), a fact constituting a phenomenon only explainable by assuming a substitution of Ti^{4+} for Si^{4+} . The general decrease of both elements with increasingly basic character is evident from the other occurrences of hyperite.

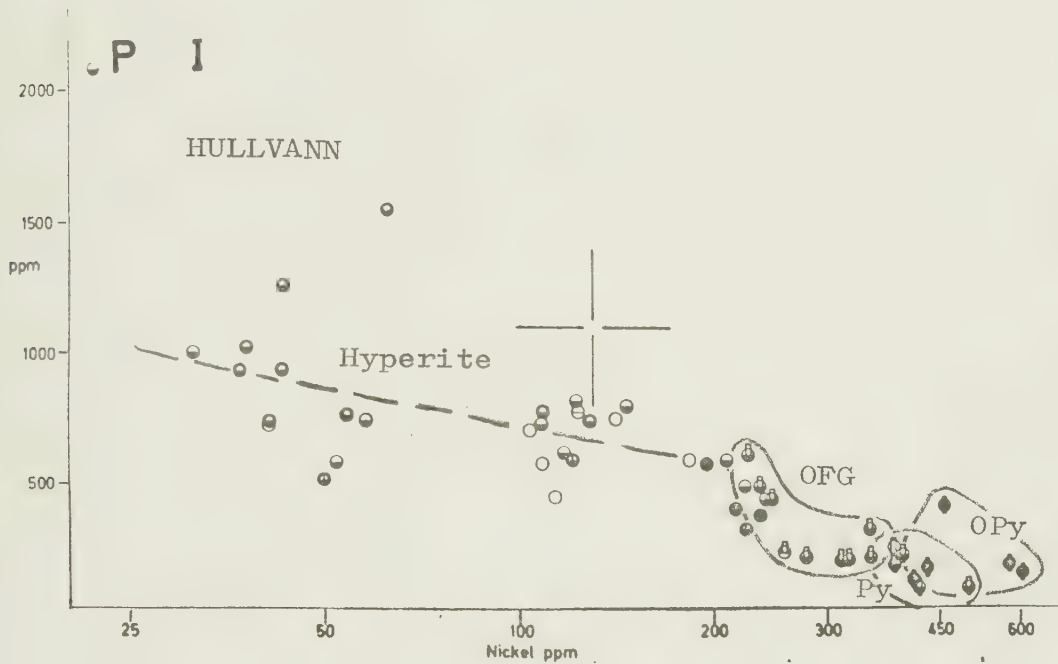




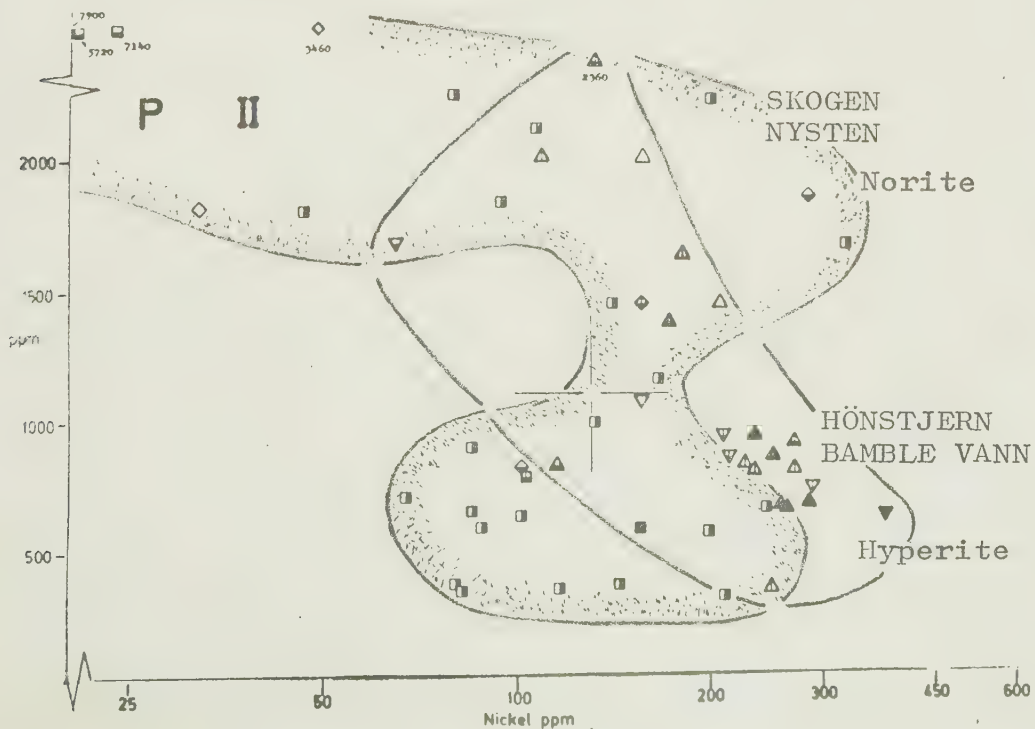
There are no clear relationships regarding the distribution of Ti and V in norite. One cause could be the especially high content of primary magnetite in this rock; this mineral is together with ilmenite generally considered to be the chief carrier of these two elements.

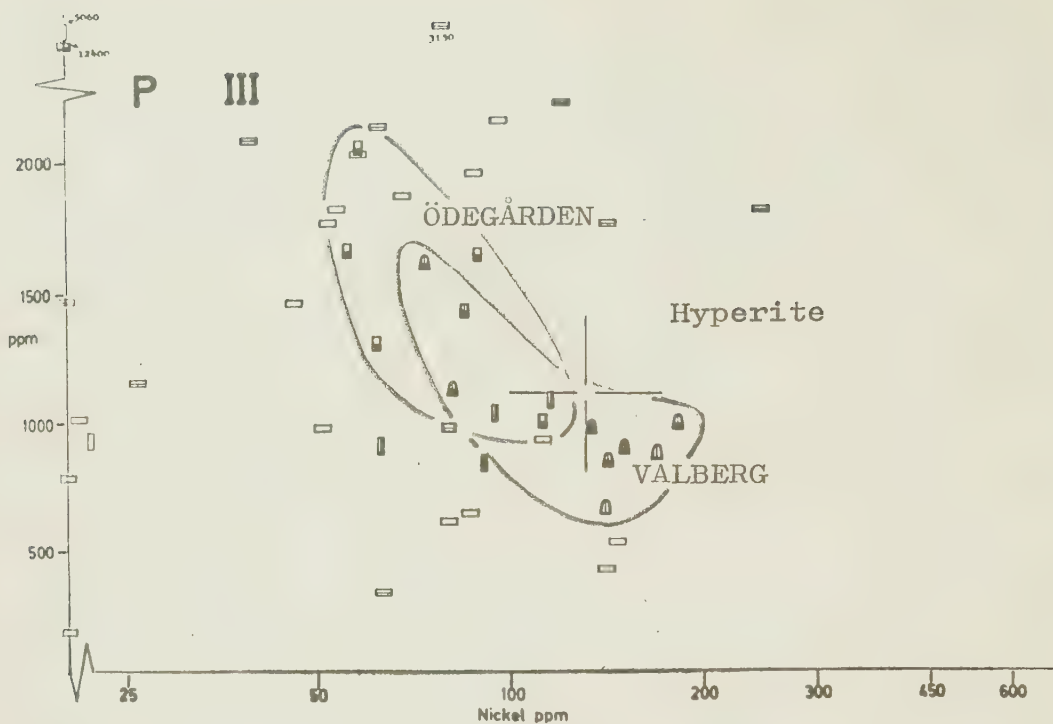
The trend towards a high and sporadic distribution with differentiation becomes most marked in the case of PHOSPHOROUS. The reason for this must be sought in the high mobility of the element, coupled with formation of the very stable mineral apatite. Although exceptions may be found, the role of P in

silicates must on a general basis, following the work of Koritnig (1965) and Henderson (1968), today be considered subordinate. The latter author recorded especially low contents in early magmatic olivine, pyroxene and plagioclase. This is reflected in the basic crystallates at Hullvann:-



The trend of P in hyperites follows that of Ti and V rather closely. This stands in contrast to norites, where the lack of correlation is even greater.

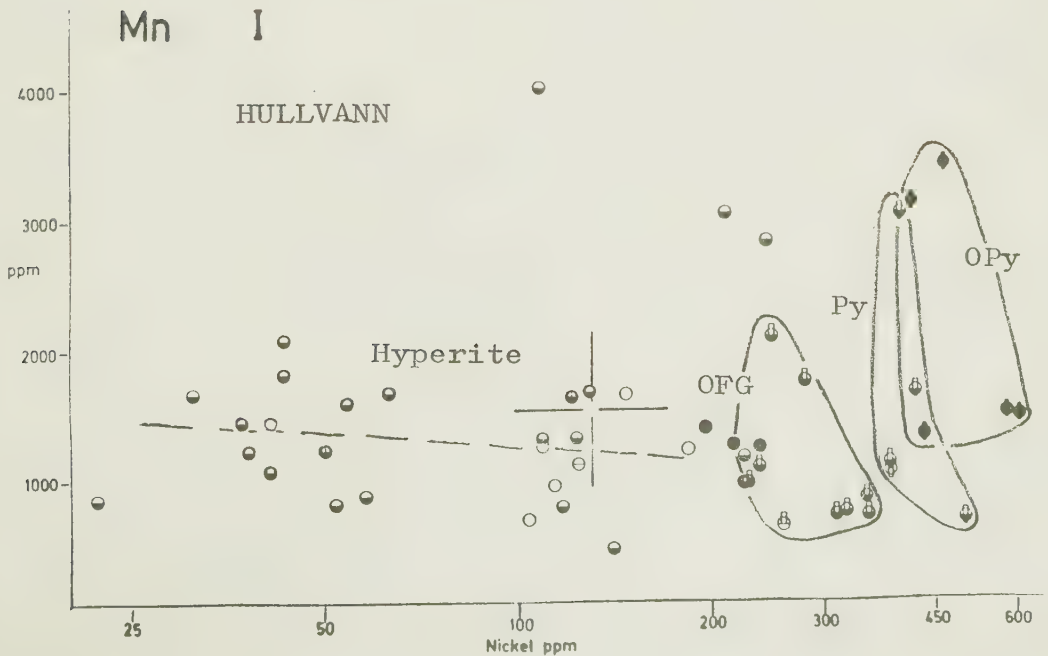
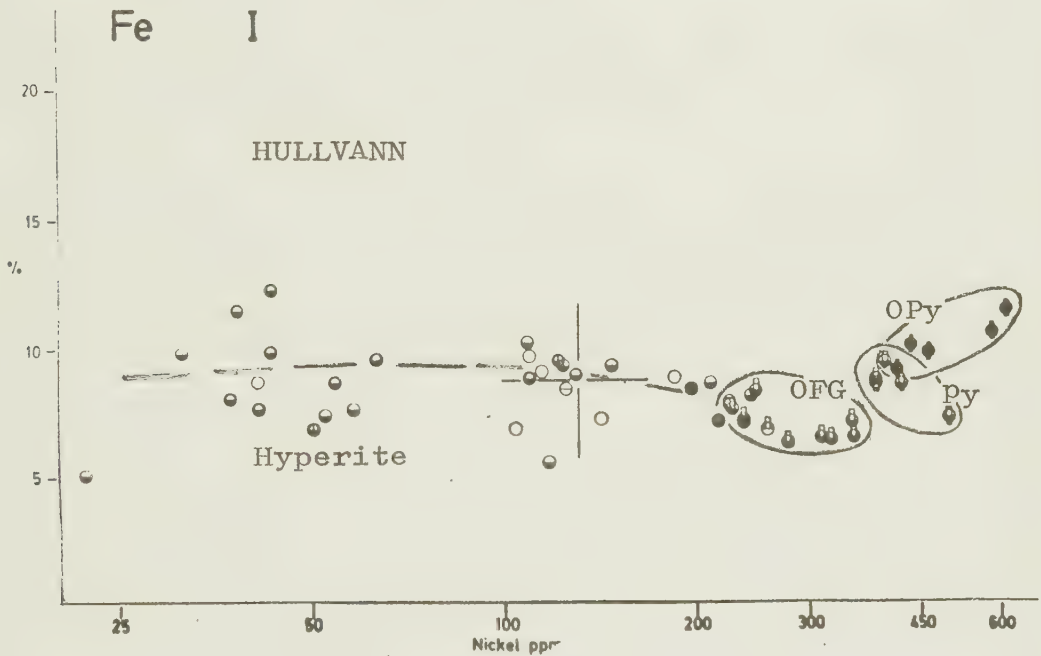




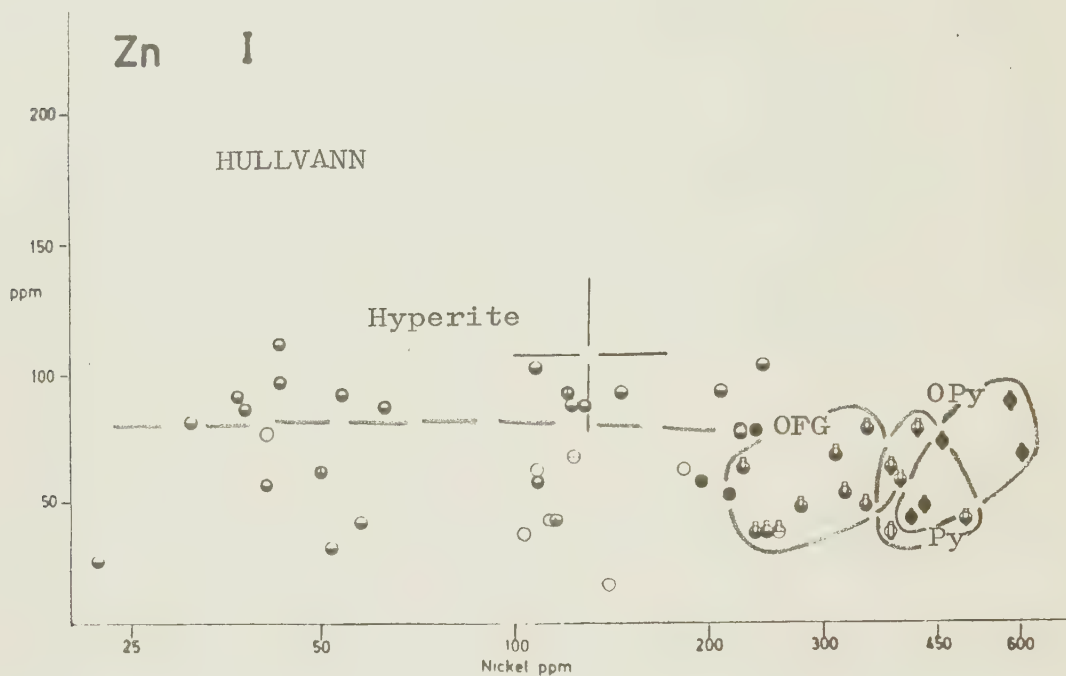
The correlation of P with basic character appears to be governed by the same principles as those valid for Ti and V. Early crystallates incorporate only small portions of these elements, whereas later gabbroic differentiates can incorporate more in their silicates when the amounts involved are not excessive. This would be expected to lead to a regular increase with differentiation as found at Hullvann. The presence of non-silicate phases, magnetite/ilmenite in the case of Ti and V, and apatite in the case of P, will greatly enhance potential accommodation. Two facts, the sporadic enrichment of certain samples in all three elements, and the presence of oxide/apatite ores of gabbroic parentage, point to a high mobility. The actual form of migration of both oxide ores and apatite is open to some doubt. The action of physico-chemically similar halogen complexes of Ti, V and P already mentioned by Bugge (1943) can, in the ubiquitous presence of F and Cl in or near the deposits at Bamble, whether as a carrier or lubricant, not be ruled out.

NON-DIFFERENTIATED ELEMENTS

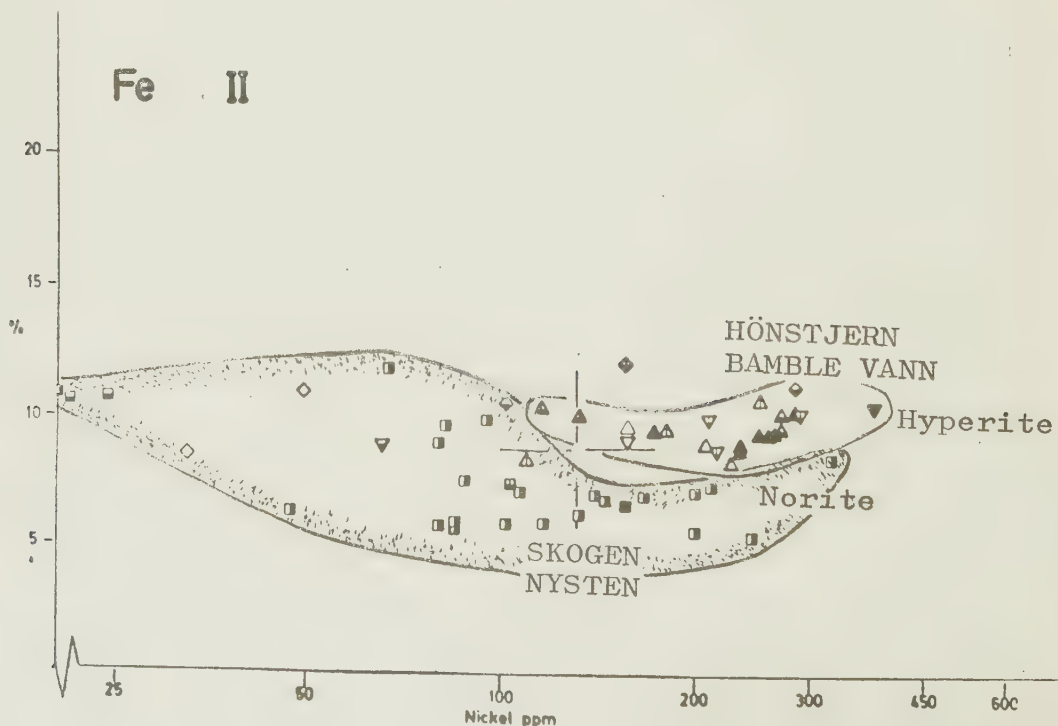
The elements IRON, MANGANESE and ZINC are maintained at a roughly constant value throughout the differentiation process. They possess the correct ionic charge (+2), and with certain reservations as to Zn also size, to be incorporated readily into all important mafic silicates. The theoretical impoverishment of Fe, Mn and Zn in the earliest members of these due to the preferential incorporation of Mg and traces of Ni and Co is counterbalanced in the pyroxenite series at Hullvann by a higher absolute proportion of them at the expense of felsic components.



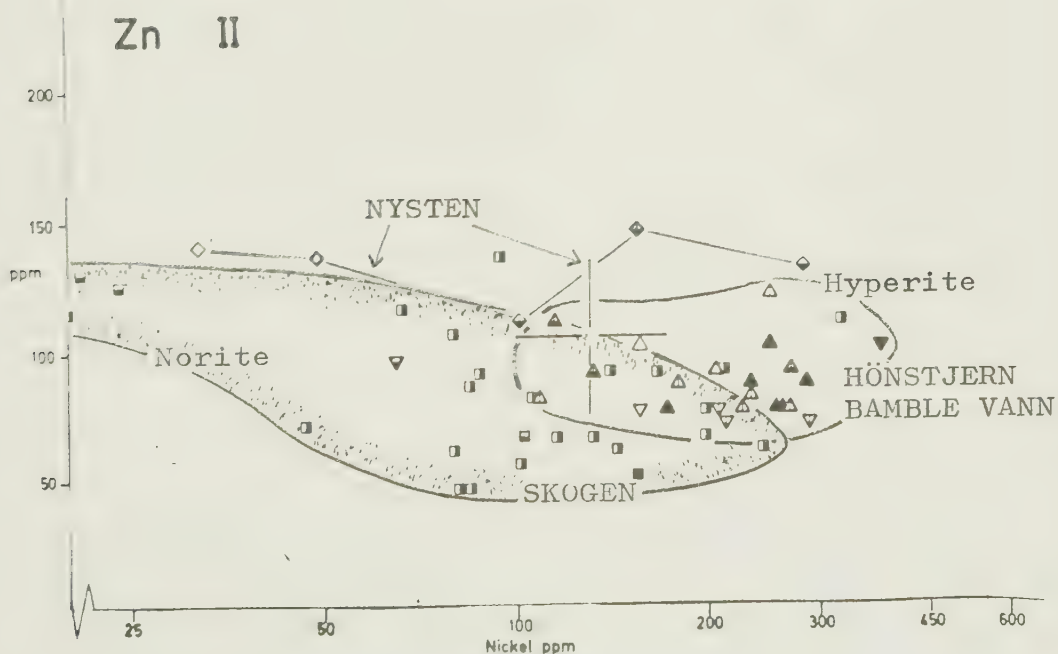
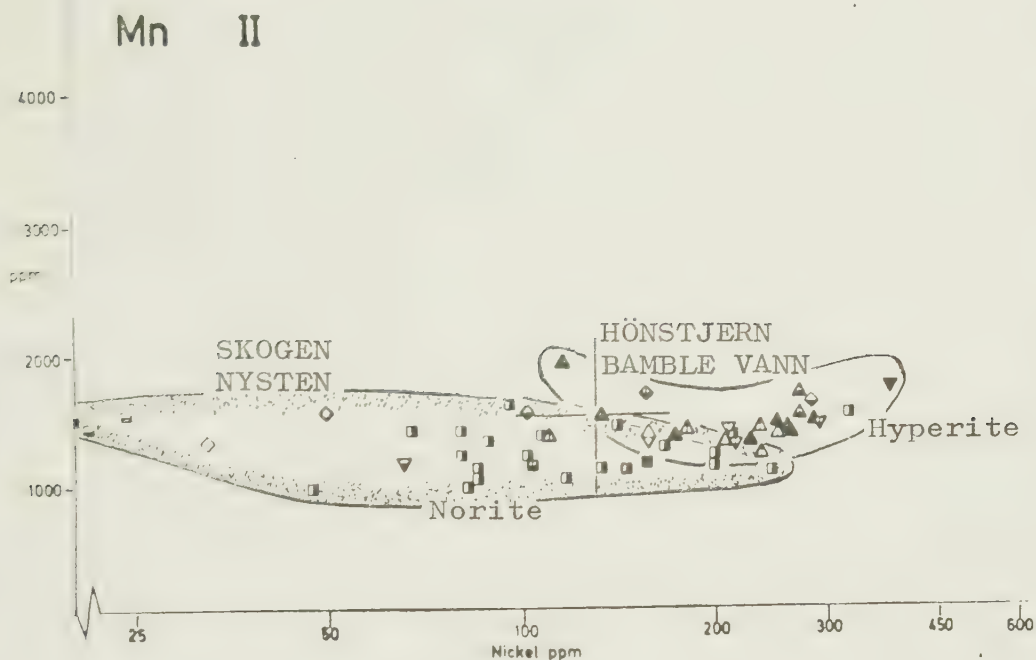
The irregularly high values of Mn in certain hyperite and pyroxenite samples could not be correlated geochemically or mineralogically. The content of Zn is somewhat below the basaltic average:-



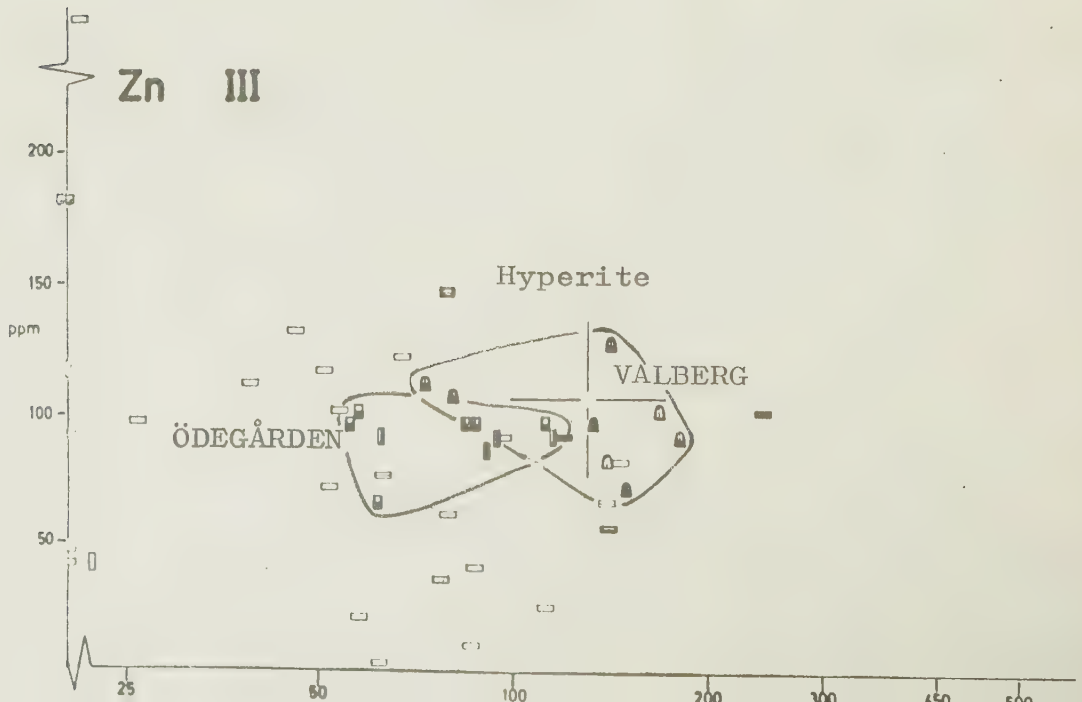
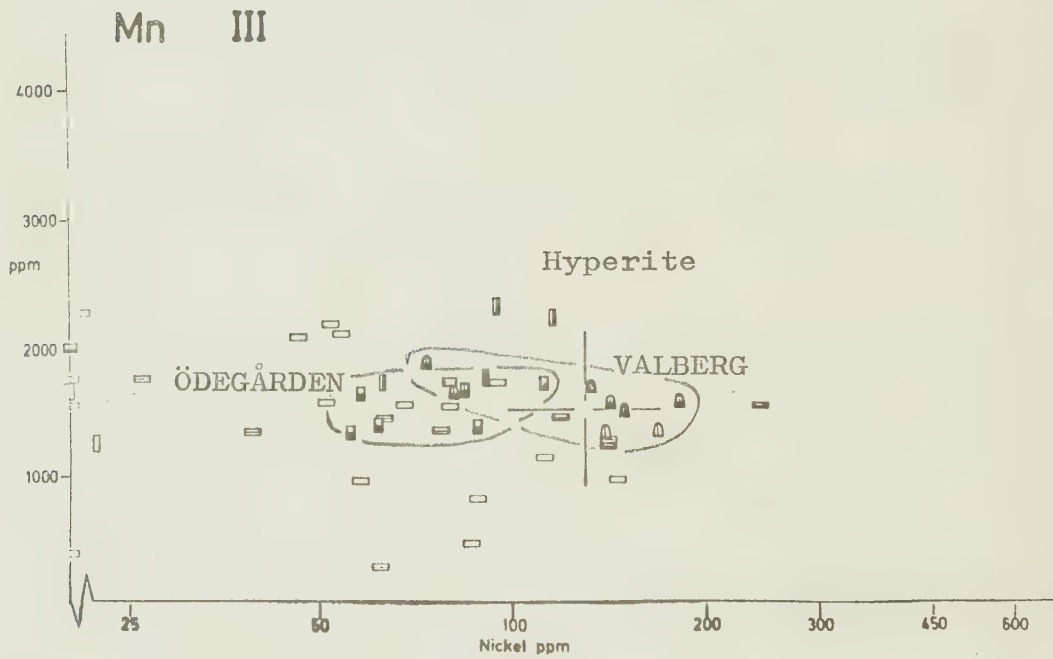
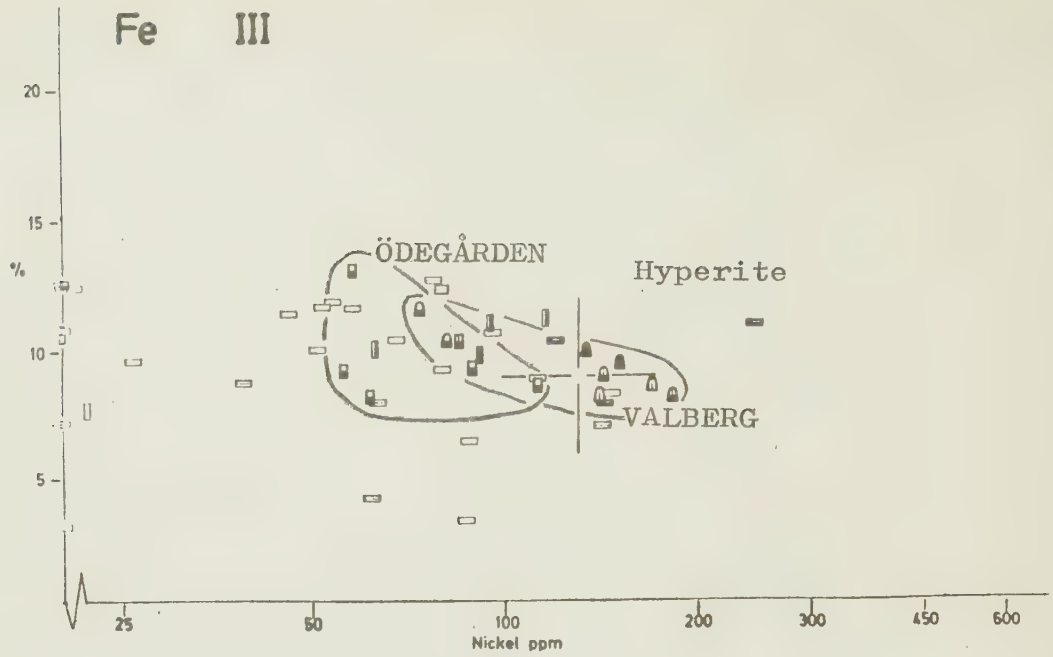
Hyperites were on average somewhat richer in Fe than norites.



This enrichment in hyperites is only just indicated in the case of Mn, and cannot really be inferred for Zn:-



The content of all three elements in the hyperite bodies at Ödegården and Valberg closely corresponded to that at Hönstjern and Bamble Vann:-



The values of all three elements remain constant in hyperites regardless of locality or basic character; in norites they differ only in the case of Fe. The relationship of Fe to Mn has often been considered linear within a group of igneous rocks (Abramovitch et.al. 1964). A general relationship of both Mn and Zn to Fe was evident in the rocks examined; the fact that Zn follows 6-coordinated Fe almost as closely as does Mn, would suggest Zn to be 6-fold coordinated in silicates, rather than 4-fold coordinated in sulphides as proposed by Neumann (1949).

Zn was enriched in the uralitized norite at Nysten and the two analysed samples from the late-stage hornblendite band at Hullvann. A high Zn content is characteristic of mafic silicates bearing OH-groups (Wedepohl 1953). This would suggest a primary origin of at least part of the hornblende.

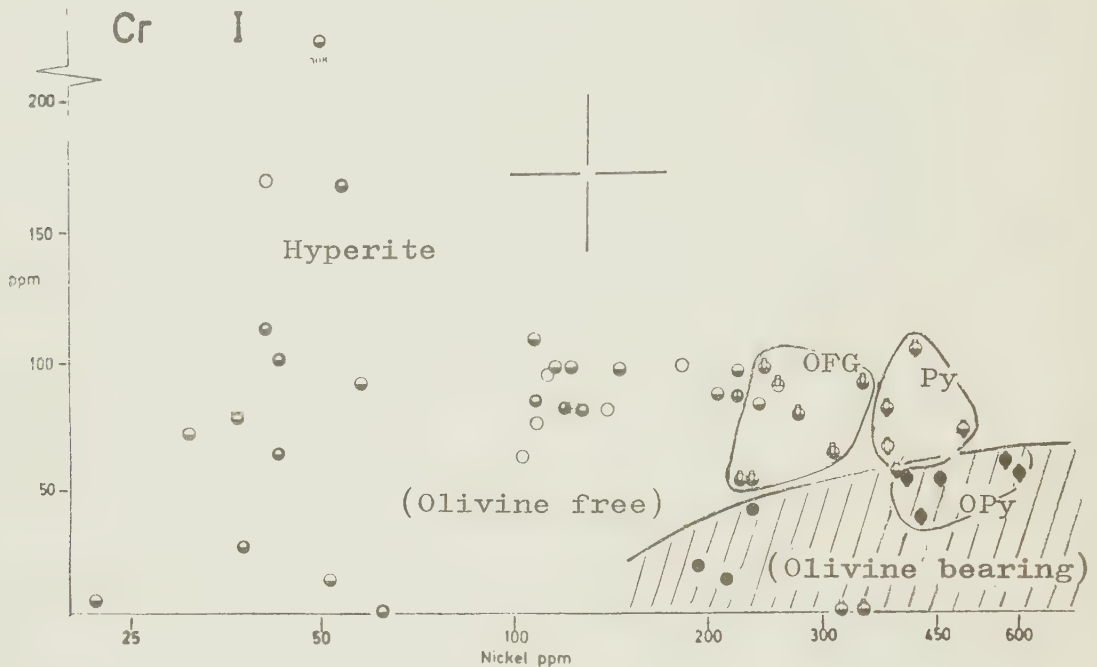
The increase of Mg, Ni and Co, and decrease of Cu, Ti, V and P with basic character in all hyperites is similar, and evident not only within individual bodies, but also among the bodies themselves. It is thus, subject to representative sampling, possible to distinguish bodies of an 'early' geochemistry (Hönstjern, Bamble Vann) from those of a 'later' one. Some bodies, such as represented by the hyperite samples at Hullvann, cover a wider range, as indeed some of the former such as at Valberg might also, if sampled more extensively. The fact that the elements Fe, Mn and Zn remain constant in spite of differentiation within and among all hyperite bodies examined, would thus indicate a co-magmatic origin.

CHROMIUM

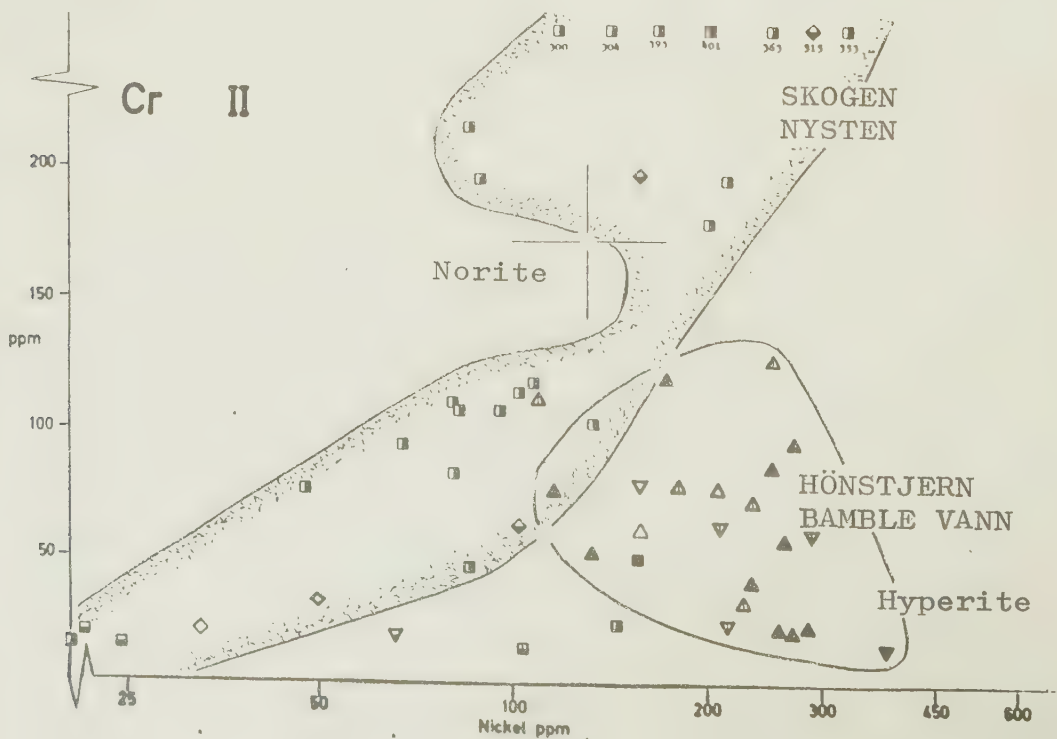
There are two somewhat contrary criteria that govern the geochemistry of CHROMIUM. The element is enriched in ultramafic rocks to a degree even greater than that of Ni, though not incorporated into OLIVINE, the most important mineral of these rocks.

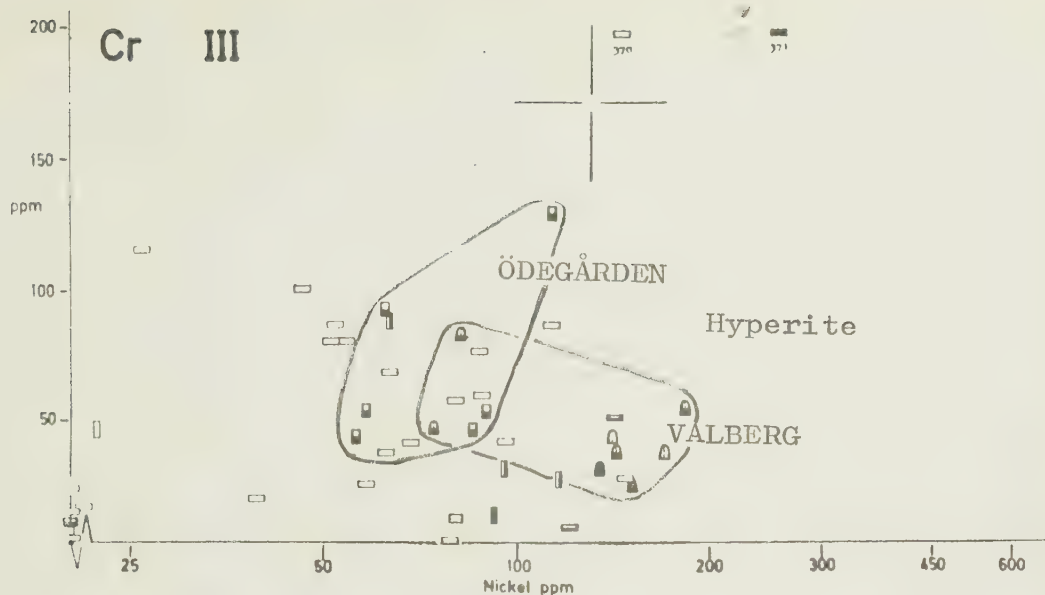
The tenors of Cr are pyroxenes, amphiboles, and oxides of the spinel group; all minerals that, unlike olivine, possess

lattice positions able to accomodate the trivalent Cr^{3+} ion. There will thus be a relative impoverishment of Cr in rocks such as at Hullvann, bearing olivine:-



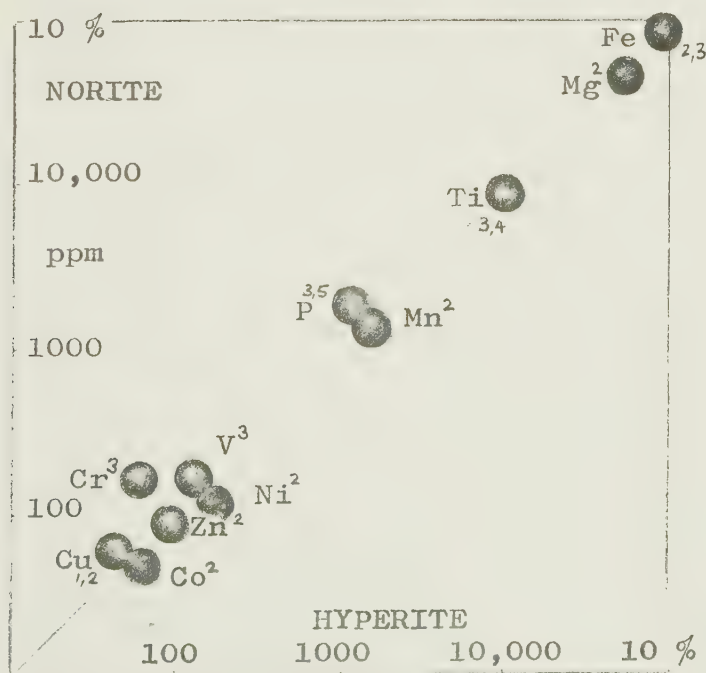
This is reflected in the other hyperites of Bamble, that exhibit a general impoverishment of Cr with increasingly basic character. In norites the place of olivine is taken by ORTHOPYROXENE, leading to an INCREASE of Cr with basic character. This, while representing the trend characteristic of basalts and basic rocks generally, stands in marked contrast to the abnormal geochemistry of hyperites:-





GEOCHEMICAL DIFFERENCES BETWEEN HYPERITE AND NORITE

The establishment of chemical averages for either rock-type will always remain subjective on account of the high degree of differentiation. The following representation derived from 37 hyperite (Hönstjern, Bamble Vann, Valberg, Ödegården) and 25 norite (Skogen, Flåtevann) analyses must therefore be considered a compromise:-



A trend already evident from the previous sections is the preferential incorporation of ions with an EVEN CHARGE in HYPERITES, and with an ODD CHARGE in NORITES.

FACTORS GOVERNING THE CRYSTALLIZATION OF HYPERITE

The preferential incorporation of specifically charged ions in the one or other gabbro type is particularly relevant in the case of Ni and Cr. Turekian (1963) found that:-

"The fractional crystallization of a basaltic magma does not result in significant alteration of the Cr:Ni ratio, indicating that this ratio is probably derived from the mantle, rather than generated by processes in the crust".

Even in tholeiitic magmas this ratio (1 : 1.3 to 1.6) remains, as shown by Greenland and Lovering (1966) relatively constant. The Bamble Hyperites are, late differentiates excepted, impoverished in Cr, but enriched in Ni with respect to the average basalt of Turekian and Wedepohl (1961). This is of interest with regard to the presence of olivine, the lattice of which cannot accomodate the trivalent ions Cr^{3+} and V^{3+} both impoverished in hyperites, but which readily accepts the divalent ones Ni^{2+} , followed by Mg^{2+} and Co^{2+} enriched in this rock. The effects of mineralogy on chemical composition would not be expected as being of consequence in rocks such as basalts, normal gabbros, and in all probability the Bamble Norites, that could all to a large degree be considered as the PRODUCT OF AN ALL-LIQUID MAGMA, but would be of prime significance in those representing wholly or in part only a CRYSTALLINE FRACTION OF A PARTLY SOLIDIFIED MAGMA.

The point at which the earliest silicates olivine and plagioclase begin to crystallize out from a basaltic magma at depth is normally impossible to decide, although it is an established fact that this can occur at some stage before the magma has finally reached the point at which the bulk of it solidifies. The solid phases differ in many properties from the liquid melt, and may be concentrated locally by such agents as gravitational settling or filter pressing. An extreme case of such action is the well defined rock TROCTOLITE, considered to represent a cumulate of early olivine and plagioclase crystals abstracted from a larger volume of basaltic magma.

It is however possible that olivine might only be enriched, without reaching the extreme case of troctolite. The chemistry of such a melt enriched in olivine would be exactly that as

actually found in hyperites: the elements Ni, Mg and Co would be increased, those not accommodated like Cr, V and Cu impoverished, being confined to the melt only.

FORMATION OF LATE-MAGMATIC CORONITES

After intrusion, the remaining melt of this partially solid mass would crystallize. Olivine however, formed under a different environment, would become unstable, and begin to react to the stable mineral pyroxene:- $\text{Mg}_2\text{SiO}_4 + \text{SiO}_2 \rightarrow \text{Mg}_2\text{Si}_2\text{O}_6$. This explains the inner corona of orthopyroxene. The SiO_2 required for this reaction must be abstracted from the surrounding feldspar, leaving an excess of Al_2O_3 . This latter factor, and the fact that some Fe and Mg from the olivine migrates out from the inner zone in the establishment of chemical equilibrium, results in the formation of the outer amphibole/spinel zone.

The fact that such zones may be of STRICTLY MAGMATIC ORIGIN is evident from the work of Stewart (1947) on the troctolite at Belhelvie in Scotland. The age of this complex is Caledonian, and definitely younger than the metamorphism of the area, so that coronite formation due to this can be absolutely excluded. Stewart (1947) describes the reaction zones as follows:-

"The reaction rims which very commonly surround the olivines of the troctolites and other rocks of the complex, when this mineral is in contact with plagioclase, are generally double, being composed of a thin colourless inner part, surrounded by a darker outer rim. The inner part consists in many cases of a colourless orthopyroxene, and in other cases of colourless amphibole. The outer part is composed of amphibole riddled with worm-like growths of another mineral. after examination of sections of the Irish rocks (described by Wager, 1932), the writer is convinced that the vermicular mineral in the Belhelvie rocks is spinel. Where pyroxene occurs, it forms either small grains or ophitic plates. Tiny flakes of biotite sometimes fringe the magnetite".

This description agrees in every detail with that of the Bamble Hyperites. Troctolitic variants of these have in fact been described (Reynolds and Fredrickson 1962, Starmer 1969).

It is conceivable that olivine crystallizes out, but fails to sink in the subjacent magma chamber. The intrusion of such a magma into higher levels will lead to a hyperite of more

normal basaltic composition, in which the olivine would still bear coronites, as formed under similar conditions as before. The present theory of PRECRYSTALLIZATION does not preclude the action of late-magmatic fluids, which are in fact essential to explain the mineral transformations found. Coronite formation, having taken place subsequent to the crystallization of all three major phases olivine, plagioclase and clinopyroxene, must be considered A LATE MAGMATIC PROCESS IN WHICH UNSTABLE OLIVINE AND MAGNETITE REACT marginally with plagioclase under the influence of residual fluids. The large number of new mineral phases formed is due to the fact that this is a process of REACTION rather than one of alteration, in which both OLIVINE (MAGNETITE) AND PLAGIOCLASE FORM SECONDARY PRODUCTS BY A MUTUAL EXCHANGE OF IONS IN THE PRESENCE OF VOLATILES SUCH AS OCCUR IN ALL MAGMAS.

Clinopyroxene appears by contrast to have been completely stable, normally occurring in large, un-corroded crystals often enclosing plagioclase ophitically. This mineral gives the appearance of having crystallized out together with at least part of the plagioclase from the remaining melt subsequent to intrusion. It is remarkably stable to alteration or reaction. Olivine crystals bordering clinopyroxene crystals are slow to react, developing only a thin rim of ortho-pyroxene. The fact that this latter mineral may at times be developed to a zone of normal thickness in the absence of an outer one, would seem not to rule out the possible action of free silica.

Concluding, it would seem that the two following factors govern the formation of coronites:-

- a. The state of disequilibrium of olivine and magnetite with the remaining phases, i.e. within the system, and
- b. The action of late magmatic fluids.

Both factors are considered essential for coronite formation, although the proportions of their influence may probably vary. Disequilibrium (a) alone could lead to a resorption of olivine with liberation of finely divided marginal magnetite as in olivine-basalts, but not to coronites containing hydrous minerals. Action of late-magmatic fluids without disequilibrium (b) of olivine would lead to serpentinization, as in the olivine pyroxenites at Hullvann.

ACTION OF METAMORPHISM ON CORONITES

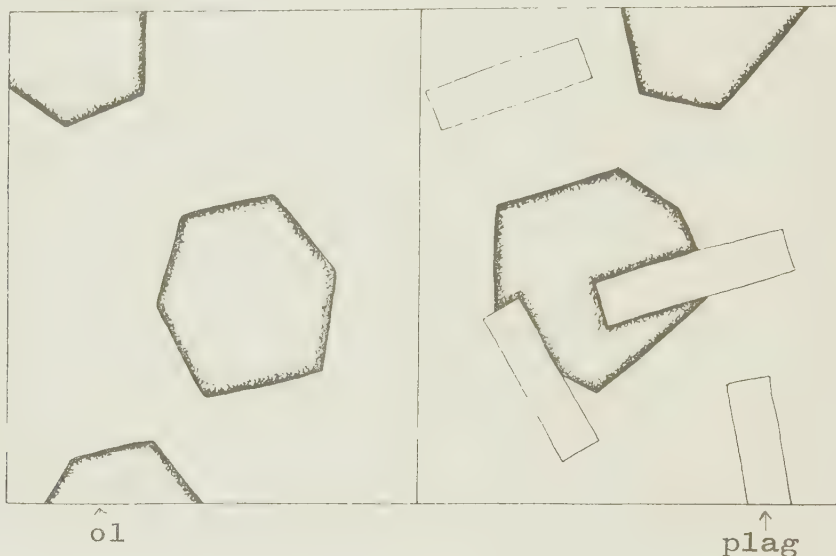
Metamorphic alteration, although not evident in the coronites examined by Stewart (1947), has affected those of the Bamble Hyperites to varying degrees. This, at first leading to a multiplicity of mineral phases, is primarily due to the fact that coronites, formed under late magmatic conditions in the presence of volatiles, may be expected as being very sensitive to increases in temperature and pressure. The first metamorphic mineral to appear is garnet, joined somewhat subsequently and eventually replaced by common hornblende. Any olivine still present at this stage will be altered to magnetite and magnesian alteration products. Garnet, magnetite and hornblende are the minerals of the Upper Almandine Amphibolite Facies, and represent those minerals into which one would expect the magmatic coronites to be transformed during the period of metamorphism that has affected the whole area subsequent to the intrusion of the gabbros.

In certain samples examined all six phases, orthopyroxene, secondary amphibole, spinel, garnet, hornblende and magnetite are present, resulting in a complex mineral assemblage which, although composed of seemingly irregular associations such as low-temperature amphibole and garnet, is now easily explainable by a logical combination of well-established processes.

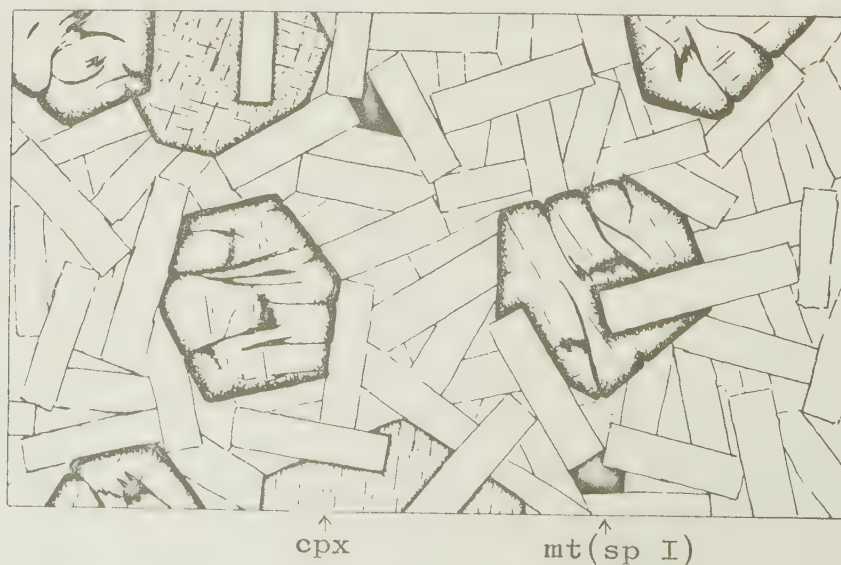
SUMMARY

The processes involved in the formation and alteration of hyperite may be presented schematically as follows:-

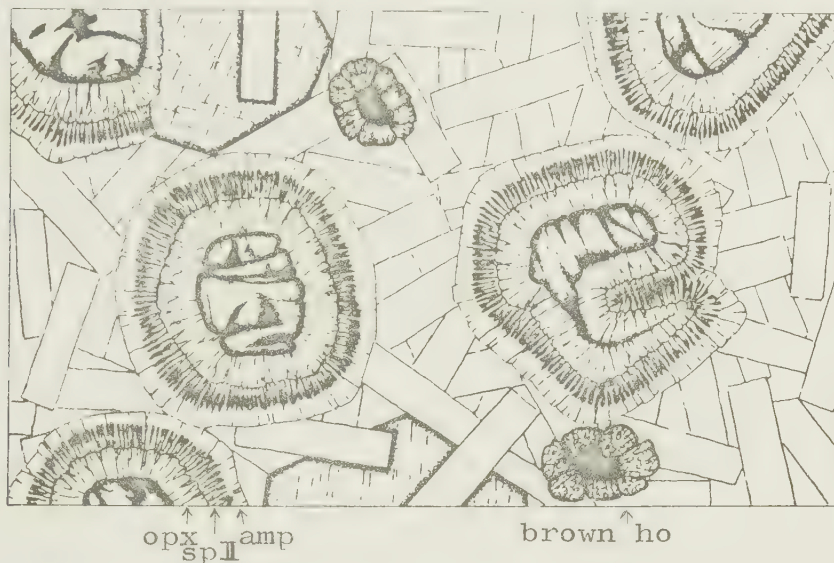
1. Depending on the composition of the basalt magma, olivine or olivine and plagioclase begin to crystallize out at depth. They may be enriched in parts of the magma chamber.



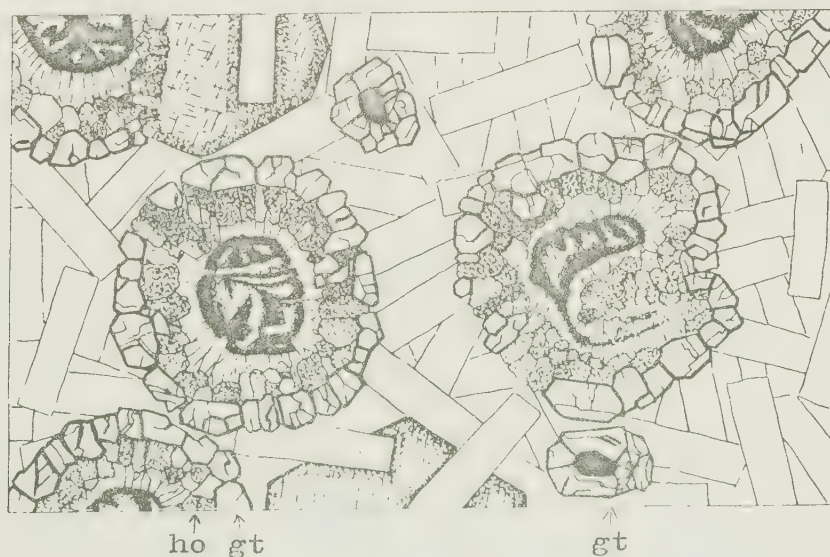
2. The resultant partly crystalline plastic mass is intruded into the final position. Consolidation results in the crystallization of the remaining liquid to plagioclase and clinopyroxene, which may be poikilitically intergrown, and magnetite. The place of the latter mineral is taken by dark green primary spinel in magnesian hyperites, suggesting that this mineral phase may already have begun to crystallize out at stage 1.



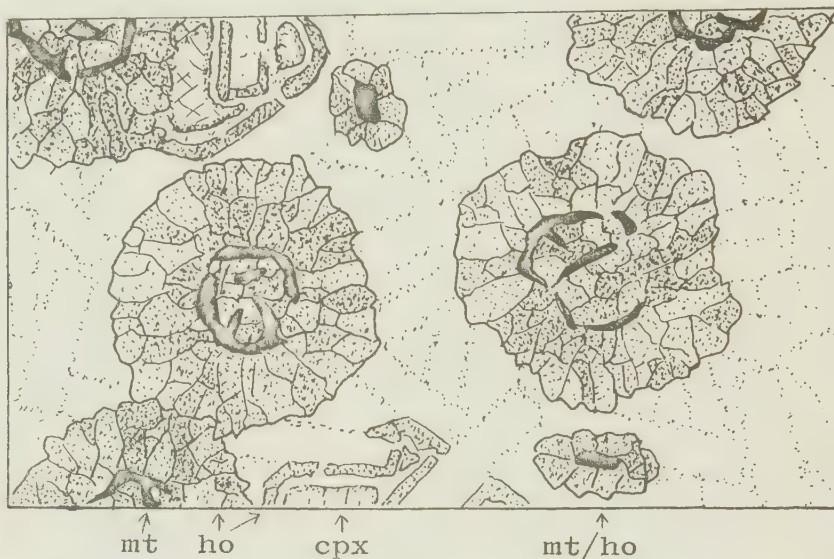
3. Following consolidation, olivine and magnetite (spinel I) react with adjacent plagioclase in the presence of late magmatic fluids that have not been incorporated into the silicate structures. The reaction products of olivine and plagioclase are orthopyroxene (inner zone) and amphibole/spinel II (outer zone) respectively. Magnetite (spinel I) and plagioclase react to brown titaniferous hornblende (and/or biotite) that can accommodate the ions of both minerals.



4. Incipient metamorphism causes alteration of the outer amphibole/spinel zone (around olivine) and brown hornblende zone (around magnetite) to garnet. This is followed by hornblendization of orthopyroxene (around olivine), and to a reduced degree also of primary clinopyroxene.



5. Further metamorphism causes a simplification of mineralogy and metamorphic convergence to an amphibolite of common hornblende, magnetite and plagioclase. Primary clinopyroxene exhibits a marked stability. The resultant rock, very characteristic of the outer zones of hyperite intrusions, may be distinguished from country amphibolites by relict masses of common hornblende, sometimes enclosing skeletal cores of magnetite representing an original olivine crystal.



Eventually this rock may itself be transformed to an ordinary equigranular amphibolite, in which chemical composition will be the only indicator of parentage.

ALTERATION OF OLIVINE SEPARATED FROM FELDSPAR

All hyperites could be assigned to some arbitrary 'stage' as above from No.3 onwards. Under special conditions, gravitational fractionation gave rise to the rock series olivine-free gabbro / pyroxenite / olivine-pyroxenite as found at Hullvann. The serpentinized state of olivine in the latter rock-type demonstrates that this mineral, once separated from feldspar, is unable to form coronites.



REFERENCES

- Abramovitch I.I., Vysokoostrovskaya E.B. and Dorofeyeva E.E. (1963), *Geochemistry*, No.7, 668.
- Ahrens L.H., (1964), *Physics and Chemistry of the Earth V*, Pergamon Press, 1.
- Batey R. (1965), Unpublished Ph.D. Thesis, University of Nottingham, England.
- Bodart D.E. (1966), Unpublished M.Sc. Thesis, University of Nottingham, England.
- (1968) *Norsk Geol.Tidsskrift*, 48, 269.
- (1969) *Z.anal.Chem.*, 247, 32.
- (1970) *Chem.Geol.*, 6, 133.
- Borisenko L.F. (1967) *Geochemistry International*, 4, 263.
- Brögger W.C. (1934) *Vid.Selsk.Skr. 1.Mat.Nat.Kl.*, 1.
- Bugge A., (1936) *Norges Geol.Undersökelse No.146*.
- (1965) *Norges Geol.Undersökelse No.229*.
- Bugge J.A.W. (1943) *Norges Geol.Undersökelse No.160*.
- Edelshtein I.I. (1960) *Geochemistry No.7*, 718.
- Ellis J. (1946) *Geol.Soc.South Africa Trans.*, 48, 103.
- Friedman G.M. (1955) *Am.J.Sci.*, 253, 497.
- Frodesen S. (1968) *Norsk Geol.Tidsskrift*, 48, 201,281.
- Gjelsvik T. (1952) *Norsk Geol.Tidsskrift*, 30, 34.
- Glaveris M. (1970) *Norsk Geol.Tidsskrift*, 50, 15.
- Greenland L. and Lovering J.F. (1966) *Geochim.Cosmochim.Acta*, 30, 963.
- Häkli T.A. and Wright T.L. (1967) *Geochim.Cosmochim.Acta*, 31, 877.
- Hegemann F. (1943) *Z.angew.Mineral.* 4, 122.
- Henderson P. (1968) *Geochim.Cosmochim.Acta* 32, 897.
- Huang W.T. and Merritt C.L. (1954) *Am.Min.* 39, 549.
- Koritnig S. (1965) *Geochim.Cosmochim.Acta*, 29, 361
- Mercy E. and O'Hara M.J. (1967) *Geochim.Cosmochim.Acta*, 31, 2331.
- Muir I.D. (1954) *Min.Mag.*, 30, 376.
- Murthy M.V.N. (1958) *Bull.Geol.Soc.Amer.*, 68, 23.
- Neumann H. (1949) *Min.Mag.*, 25, 575.
- Ricke W. (1960) *Geochim.Cosmochim.Acta*, 21, 35.
- Reynolds R.C. and Fredrickson A.F. (1962) *Geol.Soc.Amer.Bull.*, 73, 59.
- Rost F. (1939) *Z.angew.Mineral.*, 2, 1.
- Ryan M.J. (1966) Unpublished Ph.D. Thesis, University of Nottingham, England.

- Shand S.J. (1945) Geol.Soc.Amer.Bull., 56, 247.
- Stewart F.H. (1947) Quart.Journ.Geol.Soc.London, 102, 465.
- Taylor S.R. (1965) Physics and Chemistry of the Earth VI,
Pergamon Press, Oxford, 133.
- Tilley C.E. (1952) Am.J.Sci. Bowen Vol. 529.
- Turekian K.K. (1963) Geochim.Cosmochim.Acta, 27, 835.
- and Wedepohl K.H. (1961) Geol.Soc.Amer.Bull., 72,
175.
- Vogt J.H.L. (1893) Z.prakt.Geol., 125.
- Wager L.R. and Mitchell R.L. (1953) Geochim.Cosmochim.Acta,
2, 217.
- Wedepohl K.H. (1953) Geochim.Cosmochim.Acta, 3, 93.

LEBENS LAUF

Geboren am 21.3.1941 in Konstanz als Sohn des Opernsängers Erich Bodart (Verst. 1959). Besuch der Volksschule in Kassel 1948-51.

Ab 1951 in England. Internate Vinehall School, Sussex 1951-54, und Wellington College, Berkshire 1954-59. Advanced Level G.C.E. Studium an den Universitäten Durham 1960-61 und London 1961-64. B.Sc. General (London) 1964 in Chemie und Geologie. Anschliessend zwei Jahre Forschung an der Universität Nottingham. Erlangung des Grades Master of Science (M.Sc) Nottingham 1966.

Ab 1966 wieder in Deutschland. Mineralogisches Institut der T.H.Darmstadt 1966-67. Ab 1967 bei Prof.Dr.K.v.Gehlen am Institut für Petrologie, Geochemie und Lagerstättenkunde der Universität Frankfurt tätig.

Meine akademischen Lehrer waren:

Die Professoren Dunham und v.Gehlen, sowie die Herren Collier, Dodd, Duffin, Ferry, Hall, Hopkins, Jenkins, Layton, Morton, Strickson und Whitten.

